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ORGANIC CHEMISTRY



By

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Revised and enlarged tenth edition

By

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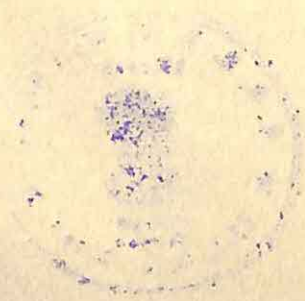
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PREFACE TO THE TENTH EDITION

The chapters have once again been revised and made up to date; this includes some current views regarding constitutions and reaction mechanisms. Increasingly greater stress has been laid on the electronic theory of valency to explain experimental observations. New matters have been incorporated here and there and a chapter on terpenes added to cover the new three-year degree course syllabuses of as many Indian universities as were available at the time of going to the press. As in the past, the author remains deeply indebted to the teachers and the students alike for their kind appreciation of and sincere support for the book. His grateful thanks are due to Dr. S. S. Subramanian, Medical College, Pondicherry, Dr. S. P. Roychoudhury, I.A.R.I., New Delhi, Dr. G. S. Saharia, Delhi University and Mrs. A. Thomas, College for Women, Trivandrum for their valuable suggestions towards its improvement. The author is also obliged to Mr. J. G. Walton, Calcutta, for his kind assistance.

Calcutta,
February, 1960.

P. B. SARKAR

PREFACE TO THE NINTH EDITION

Except some minor additions and alterations here and there, the present edition is practically a reprint of the last edition. Advantage has been taken, as before, to make the text up to date. In spite of best efforts, a few misprints have possibly escaped notice. I regret for this and crave the indulgence of my readers. I owe a debt of gratitude for some valuable suggestions to Profs. K. Krishna Rao, M.Sc., Scott Christian College, Nagercoil, I. D. Ojha, M.Sc., L. T., Meerut College, Meerut, N. K. Basu, M.Sc., B. N. College, Patna, and Mr. M. Abu Hena, Belfast.

Calcutta,
May, 1957.

P. B. SARKAR

PREFACE TO THE EIGHTH EDITION

The chapter on atomic structure and electronic theory of valency has been re-written to make it more comprehensible. A new chapter on the mechanism of organic reactions has been introduced. Attempts have been made to explain the more important facts of organic chemistry in terms of the electronic theory. This will help the students to grasp more clearly the fundamental principles of modern organic chemistry. The current syllabuses of some universities have also been covered. It is not, however, claimed that this little volume contains everything, no text-book possibly can.

The task of revision has been somewhat easier for the valuable suggestions received from many friends; the author's grateful thanks are due to them all. He is particularly indebted to Dr. M. M. Bokadia, B. R. College, Agra, Dr. P. K. De, Principal, State Agricultural

College, Calcutta, Prof. N. Chakravarthi, Madura College, Prof. N. R. Aggrawal, D. M. College, Moga, Prof. N. L. Jain, D. Jain College, Baraut, Prof. B. N. Puruthi, G. M. N. College, Ambala Cantt., Prof. T. S. Ramabhadran, Government Victoria College, Palghat.

P. B. SARKAR

Calcutta,
May, 1955.

PREFACE TO THE SEVENTH EDITION

Changes, based on suggestions so kindly given by professors, have been made, keeping the volume constant. If the book has proved useful to the students, it is largely due to this hearty co-operation, offered ungrudgingly, during the last 12 years. Words are inadequate to express my gratitude. I fervently hope that friends will kindly continue the favour in future.

I am particularly indebted to Prof. P. B. Panicker, Pachaiyappa's College, Madras, Prof. A. K. Ghose, St. Xavier's College, Ranchi, Prof. P. N. Langer, M. B. College, Udaipur, Prof. S. N. Paul, St. Anthony's College, Shillong, Dr. K. I. Kuriyan, S. N. College, Quilon, Prof. G. D. Advani, B. V. B. College, Andheri, Prof. K. M. Lahiri, St. Columbas' College, Hazaribag, Prof. N. K. Basu and Prof. J. C. Banerji, B. N. College, Patna, Prof. S. L. Sareen, N. R. E. S. College, Khurja, Prof. N. C. Deb, M. B. B. College, Agartala, and Prof. N. P. Mookherjea, Dungar College, Bikaner.

Calcutta,
May, 1953.

P. B. SARKAR

PREFACE TO THE SECOND EDITION

The work has been revised and much new matter has been added. The latter includes a short account of the electronic theory of valency, resonance structure, optical activity of organic compounds having no asymmetric carbon atom, the Fischer-Tropsch process, etc. The chapter on amino-acids has been enlarged and that on proteins re-written so as to be more informative.

I am very much obliged to those who have been kind enough to send in their appreciation of the book. For pointing out some errors and misprints and also for offering valuable suggestions, I am indebted to Dr. S. V. Anantakrishnan (Tambaram), Principal B. B. De (Madras), Mr. C. R. Nodder, Dr. S. V. Shah (Kolhapur), Mr. G. C. Roy (Rangpur), Mr. M. Q. Doja (Patna), Dr. K. I. Kuriyan (Annamalainagar), Dr. A. C. Sircar (Calcutta), Principal H. Krall (Agra), Mr. N. K. Basu (Patna), Father J. Van Neste (Calcutta), Mr. Ram Prasad (Gwalior), Mr. D. C. Roy (Calcutta), Mr. H. L. Rohatgi (Cawnpore), Mr. B. K. Banerjee (Rajshahi), Mr. S. Ramchandran (Rajamundry) and Mr. N. L. Mukherjee (Jaipur).

Calcutta,
May, 1943.

P. B. SARKAR

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INTRODUCTION

Historical survey.—Substances like oils, fats, sugar, starch, gums, resins, vinegar, spirit, etc., were well known to the ancient people; they were also acquainted with the process of making soaps from oils and fats, and the art of dyeing fabrics with indigo, madder root or Tyrian purple. All these were obtained directly or indirectly from plants or animals which were believed to possess 'organised structure'. In order to distinguish them from substances of mineral origin, or those derived from non-living sources, they were called *organic*. More than 2,000 years ago, the Hindus recognised organic compounds as distinct from inorganic, and classified the former under two heads, *viz.*, (i) vegetable substances, *e.g.*, molasses, fermented liquors, fruit acids, saps, juices of plants, etc., and (ii) animal substances such as milk, honey, fat, bile, etc. In the pre-Buddhistic era, Charaka even distinguished between animal and vegetable oils (Hindu Chemistry by P. C. Ray, Vol. II). C. W. Scheele (1742-86), a Swedish apothecary, isolated several acids, *e.g.*, oxalic, malic, citric, tartaric, gallic acids, etc. from plants. In 1747 Marggraf discovered beet-sugar and showed that it was the same as cane-sugar known long ago. In 1732 Boerhave reported urea in urine. The great French savant, A. L. Lavoisier (1743-94), accurately analysed a large number of organic substances and showed in 1784 that *all* of them contained carbon and sometimes nitrogen, besides hydrogen and oxygen. In view of the complex nature of organic compounds and their occurrence in the living world, it was widely believed that they were produced under the influence of some mysterious force, called 'vital force' (Latin *vita* life), inherent in living organisms. To prepare them artificially in the laboratory was considered impossible. This view was supported by the fact that whereas an inorganic compound such as sodium chloride could be obtained directly from the elements, an organic substance, *e.g.*, ethyl alcohol, C_2H_5O , could not be formed by combining the three elements. J. Berzelius (1779-1848), a leading Swedish chemist, tenaciously upheld this theory of vital force.

In 1828 F. Wöhler (1800-82), a German pupil of Berzelius, accidentally obtained urea, a typical product of animal metabolism, by evaporating an aqueous solution of ammonium cyanate, an inorganic salt (but both ammonia and cyanic acid, from which he prepared ammonium cyanate, were then obtained from animal source):



Wöhler wrote to Berzelius, "I must tell you that I can make urea without the need of kidneys or of any animal whatever." This gave a rude shock to the vital force theory which received a death blow from H. Kolbe who synthesised, *i.e.*, made artificially, acetic acid from its elements in 1844. Many other syntheses that followed (Berthelot

synthesised methane in 1856) made the vital force theory absolutely untenable. It was recognised beyond all doubt that the *same* chemical forces operated in the organic and inorganic worlds—the *same* laws of combination governed the formation of both types of compounds. That there exists no sharp line of demarcation between organic and inorganic chemistry was conclusively proved and universally accepted.

During the first half of the nineteenth century, organic chemistry was in its infancy, being mainly a chemistry of analysis. With the accumulation of a large number of compounds, schemes of classification were adopted, which eventually led to theories of molecular structure later on. In the sixties of the nineteenth century, a great impetus was given to organic chemists by Kekulé's theory on the structure of organic compounds. As a result, organic chemistry reached the synthetic stage during the second half of the last century. Since then the development of the science has been rapid, continuous and almost phenomenal.

Organic chemistry is essentially the chemistry of compounds of carbon. The distinction between the two branches of chemistry—organic and inorganic—though arbitrary, is still retained for the sake of convenience. One whole branch of chemistry has been allotted to a single element carbon, out of ninety-eight known elements in the Periodic Table, for several grounds *viz.*, (i) The total number of organic compounds so far discovered and synthesised is already vast—about 10 lacs—whereas compounds of all the other elements come to about 75 thousand. (ii) Organic compounds are related to one another in a striking manner and possess certain characteristic properties not generally found in the organic group. For example, all alcohols behave more or less similarly; at high temperature all organic compounds decompose while most of the inorganic compounds are quite stable. Organic substances readily dissolve in organic solvents like alcohol, benzene, etc., while inorganic substances are, as a rule, insoluble in them, etc., etc. (iii) Many organic molecules are complex—far more complex than inorganic ones. Soluble starch is believed to possess the molecular formula $C_{1200}H_{2000}O_{1000}$ and the molecular weight of cotton cellulose has been found to be about five lacs. Protein molecules have mostly eluded elucidation up till now. (iv) A large number of organic compounds with widely different properties may have the *same* molecular formula; thus, $C_{10}O_3H_{13}N$ stands for 135 compounds. $C_{10}H_{22}O$ represents 507 compounds, while for $C_{20}H_{42}$, there are 366,319 theoretical possibilities and for $C_{30}H_{62}$ as many as 4,111,846,763! This is practically unknown amongst the compounds of other elements. (v) By virtue of its atomic structure and its position in the Periodic Table, carbon possesses an extraordinary capacity for combining with other carbon atoms and elements like oxygen and hydrogen; hundreds or even thousands of carbon atoms may occur in a single molecule, joined each to each; but in an inorganic molecule, the number of atoms of any element is usually very small and they are seldom joined each to each. (vi) Carbon compounds are composed of only a few other elements, *viz.*, hydrogen,

oxygen, and sometimes nitrogen, sulphur and phosphorus. The rest of the elements are conspicuous by their absence in organic compounds. (vii) Organic reactions are mostly non-ionic and proceed rather slowly whereas inorganic reactions are mostly ionic and rapid.

Ever since chemists began to delve into the enigma of life from the chemical point of view, organic chemistry became rather important. Its intimate relation with vital processes makes it difficult to distinguish from biochemistry and physiology. The synthesis of atropine, atabrine and sulphanilamide in the organic laboratory has contributed much towards the progress of pharmacology.

As regards the application of organic chemistry, we may mention the innumerable manufactures which have been developed. Dyes, cosmetics, soaps, drugs, spirits, etc. have added to the comfort of the civilised world. Synthetic rubber, synthetic plastics like bakelite, artificial silk (e.g., nylon) and wool, perfumes, power alcohol are all from the organic laboratory. The discovery of vitamins and hormones has given a new stimulus to the study of organic chemistry, resulting in the synthesis and commercial production of many. We now have a number of antibiotics such as penicillin, streptomycin and chloromycetin, which have given great relief to the suffering humanity.

Organic compounds are obtained in bulk mainly from mineral sources such as coal tar, petroleum, oil shale, etc.; the plant world supplies starch, oils, cellulose, sugars, resins, alkaloids, etc. in abundance. From the animal kingdom are derived proteins, fats, some sugars, hormones, etc. But by far the largest number of them have been synthesised in the laboratory by the organic chemist.

CHAPTER I

PURIFICATION OF ORGANIC COMPOUNDS

The behaviour of organic compounds is studied mainly in the light of molecular structure. As the first step in determining structure, a substance is analysed, qualitatively and quantitatively, in the purest possible state. Purification of organic compounds is not always easy and different methods, depending upon the nature of the compound and impurities, are employed.

Crystallisation is the commonest way of purifying most organic solids. A substance A can be separated from impurity B by filtration, when a suitable solvent is found that dissolves either A or B. In case A and B are unequally soluble, say, for instance, if B is more soluble than A, A can be obtained pure by several re-crystallisations, B will remain in solution. In case A is more soluble than B, due to its much higher proportion, A will crystallise first, the quantity of B being insufficient to saturate the solvent. A hot, saturated solution of the mixture is allowed to cool. A crystallises out first and obtained in a purer state. It is further purified by recrystallisation. By *fractional crystallisation*, A and B are separated. The temperature co-efficient of the solubilities of organic compounds is generally high.

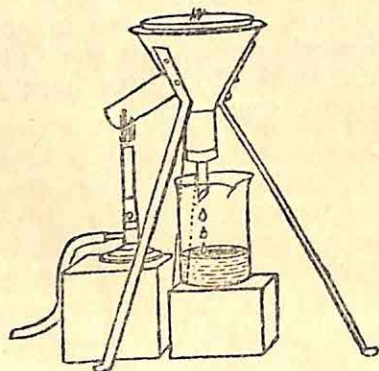


Fig. 1. Hot filtration.

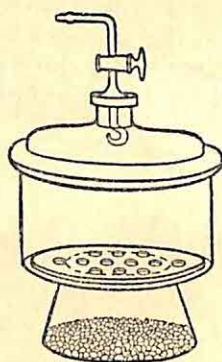


Fig. 2. Desiccator.

The mixture is dissolved in the minimum quantity of the boiling solvent and filtered hot. To prevent crystallisation during filtration, a funnel with a hot-water jacket may be used (Fig. 1). Large crystals appear on slow cooling. Sometimes supercooling prevents crystallisation; in such a case crystallisation is started either by sowing with a small crystal of the solute, or by scratching the sides of the container with a rounded glass rod. A Buchner funnel and a water pump (Fig. 3) make filtration much quicker. The crystals are washed once or twice with a little of the cold solvent, dried in the steam- or air-oven and kept in the desiccator (Fig. 2), preferably under vacuum, if the substance is volatile or hygroscopic.

Crystallisation is repeated until the solid has the *same* melting point on two successive crystallisations. Water, alcohol, ether, petroleum ether, benzene, glacial acetic acid, acetone, carbon tetrachloride, chloroform, etc., are common solvents. A mixture of two solvents,

e.g., alcohol-ether, alcohol-benzene, etc., is sometimes more suitable than a single. A suitable solvent has to be found by trial and failure. Separation from inorganic impurities is rather easy inasmuch as the latter are, as a rule, insoluble or nearly so, in common organic solvents. Water which dissolves most inorganic, but few organic compounds, may serve the purpose. The solvent must not obviously react chemically with the substance to be purified.

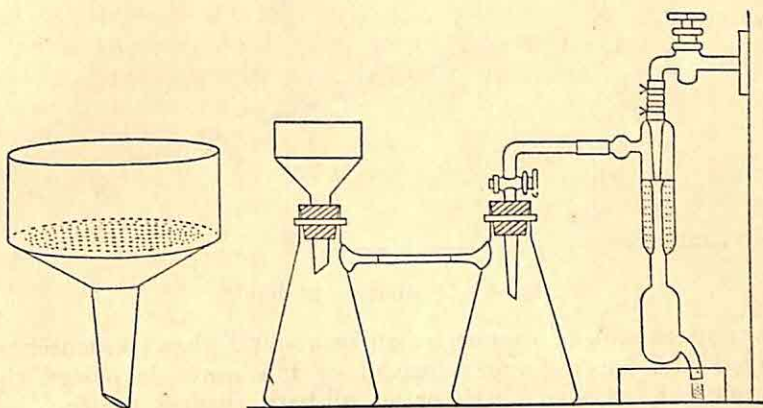


Fig. 3. Buchner funnel and filtration under reduced pressure.

Sublimation.—Some organic solids, having a relatively high vapour pressure, vaporise on heating without liquefaction, *i.e.*, they sublime. They can, therefore, be purified from non-volatile impurities by sublimation. The sample is heated on a porcelain basin, covered with a funnel with its stem closed with cotton wool (Fig. 3a). The sublimate deposits on the inner wall of the funnel and is removed. Camphor, naphthalene, etc., are thus obtained pure. Substances like indigo, which sublime with decomposition at ordinary pressure, may be sublimed under reduced pressure.

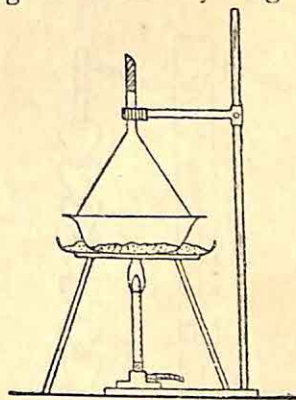


Fig. 3a. Sublimation.

Distillation.—If a liquid has nonvolatile impurities, it may be easily purified by distillation (Fig. 4). When two or more organic liquids occur together, the common way of separation is by distillation. If their boiling points (b.p.) are fairly apart, a simple distillation is sufficient. On heating, the most volatile component boils first. The temperature remains steady while most of this liquid passes over and is obtained practically pure. It rises again until the b.p. of the next component is reached. Benzene (b.p. 80.4°) can thus be easily separated from nitrobenzene (b.p. 209°). An air-condenser is used generally for liquids boiling above 130° . To avoid bumping, a few small pieces of unglazed porcelain may be added to

the distilling flask; the vapour forms bubbles on the rough surface of the latter. Superheating and so bumping is thus prevented. For

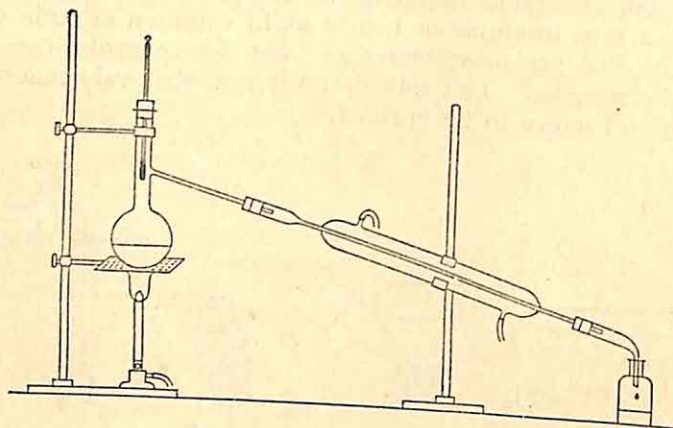


Fig. 4. Distillation of liquids.

better condensation of vapour, a ball or a spiral glass condenser may be employed and ice-cold water instead of tap water is passed through the condenser. A water-bath or an oil-bath ensures uniform heating.

When the boiling points of the components lie close, they are separated by distillation with a fractionating column (Fig. 5) which is inserted *vertically* between the distilling flask and the condenser. The principle may be better explained by an illustration. Suppose we have a mixture of A and B, boiling at 90° and 100° respectively. On heating, the vapour that issues contains a larger proportion of A than does the original mixture. When this is partially cooled in its upward passage, B condenses more rapidly than A; as a result the vapour that goes up, gets still richer in A. As it rises higher and higher, it becomes richer and richer in A. The condensed liquid deposits in the constrictions and drops back to the distilling vessel. The ascending column of vapour is thus steadily 'scrubbed' by the descending liquid; the longer the fractionating column, the better the separation. The distillate in the receiver consists mostly of A and some of B. The process is repeated until separation is complete. Industrial purification of alcohol (b.p. 78.5°) from water (b.p. 100°) is based on this principle.

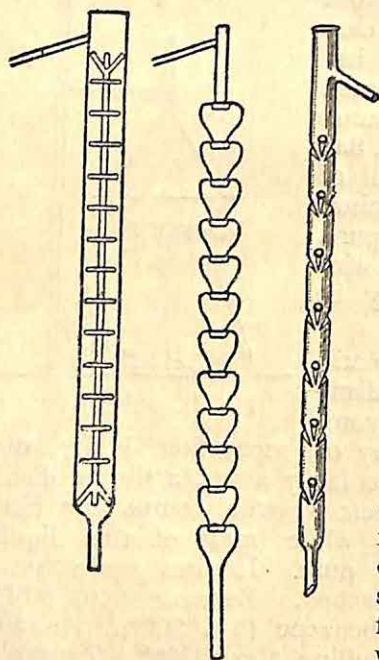


Fig. 5. Fractionating columns.

Distillation in vacuum.—Many organic liquids decompose at, or below, their boiling points. These are purified by distillation under reduced pressure. When the pressure is lowered, the boiling point falls correspondingly and decomposition is avoided. Glycerol, for example, boils at 209° with decomposition at atmospheric pressure but distils undecomposed at 180° under 12 mm. pressure. An arrangement shown in Fig. 6 is usually employed for this purpose. A receiver, having a side-tube, is attached air-tight to a condenser and connected through a manometer to a pump. A water-pump ordinarily serves the purpose, but for very low pressure or vacuum, an oil pump must be used. Different fractions can be collected without disturbing the arrangement.

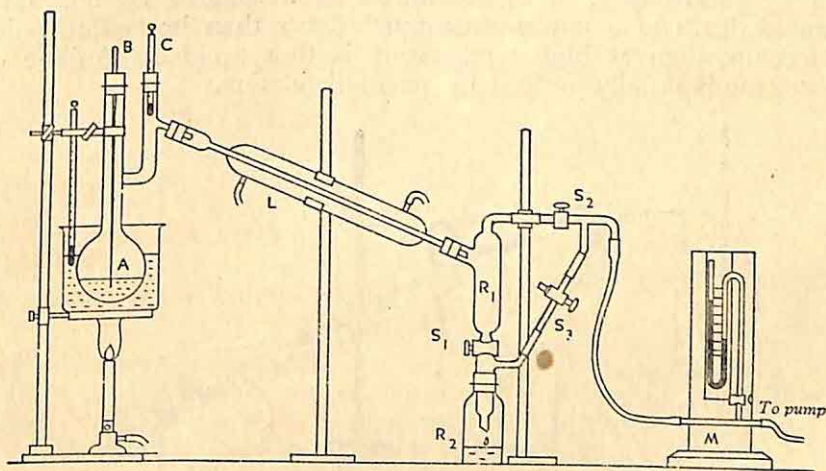


Fig. 6. Distillation under reduced pressure.

A is a Claisen's distilling flask, specially designed to stop overflow of liquid by bumping. B, a capillary tube, prevents bumping by ensuring uniform boiling. C is a thermometer, L, a Liebig condenser and R_1 , a receiver. S_1 , S_2 and S_3 form a triangle of stop-cock arrangement by which, keeping the vacuum of the system intact, R_2 , in which the liquid collects, can be changed. M is a manometer.

The liquid to be distilled is dehydrated by thoroughly shaking with fused calcium chloride, quicklime, solid caustic potash or anhydrous potassium carbonate, depending upon the nature of the liquid. Thus acids cannot be dehydrated with caustic potash, and alcohol with calcium chloride.

Liquids that form constant-boiling (or azeotropic) mixtures cannot be separated by fractional distillation. The excess of either constituent over the constant-boiling proportion, distils and as soon as the azeotropic composition is reached, the mixture passes over. Thus 4.43% of water (b.p. 100°) forms with 95.57% of alcohol (b.p. 78.5°) a mixture which boils at 78.15° ; 67.64% of benzene and 32.36% of alcohol give a similar mixture boiling at 68.25° .

Molecular distillation is carried out under 0.0001 mm. to 0.01 mm. of mercury range in specially designed stills which have the condensing surface and the evaporating surface within the mean free

path of the molecules to be distilled. The distillation temperature under such high vacuum falls considerably, sometimes by about 300° . High-molecular compounds or compounds having very high boiling points can thus be separated or purified.

Steam-distillation is done when a compound, insoluble in water, is volatile in steam but its impurities are non-volatile. Essential oils such as rose oil (or eucalyptus oil) can thus be extracted from the flowers. The substance with a little water (if it is a solid but not otherwise) is placed in a flask F (Fig. 7) which is attached to a condenser and heated. A current of steam from the vessel B is led into the liquid in F. The distillate in the receiver R is a mixture of the volatile organic substance and water, which can be separated with a separating funnel (Fig. 8) or by means of a suitable solvent. The compound distils at a temperature much *lower* than its boiling point and decomposition at high temperature is thus avoided. Aniline or nitrobenzene is usually purified by steam-distillation.

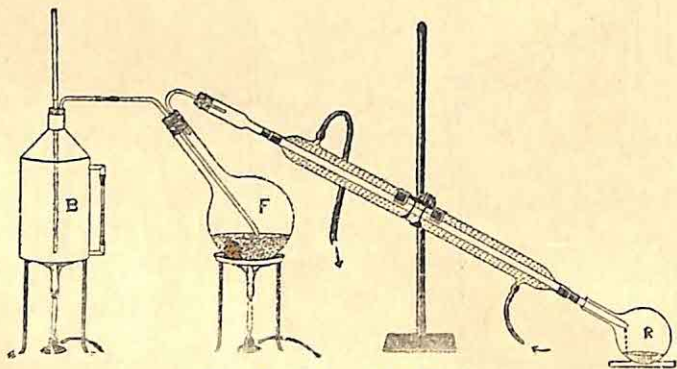


Fig. 7. Steam-distillation.

The proportion of water and the substance in the distillate may be calculated. If B is the atmospheric pressure at the time of distillation,

$B = p_1 + p_2$, where, at the temperature of distillation,

p_1 = partial pressure of water-vapour and

p_2 = partial pressure of the substance.

If m_1 and m_2 are mol. wts. of water and the substance respectively,

$\frac{w_1}{w_2} = \frac{m_1 \times p_1}{m_2 \times p_2}$, where w_1 and w_2 are weights of water and substance respectively in the distillate.

Or, $\frac{w_1}{w_2} = \frac{18 \times p_1}{m_2 \times (B - p_1)}$ (18 = mol. wt. of water).

B and p_1 are obtained from the barometric height and standard tables respectively.

By passing superheated (i.e., high pressure) steam, p_2 relative to p_1 is raised; w_2 increases correspondingly. This means that we now have a higher proportion of the organic compound in the distillate.

Separation with solvents.—A mixture of two liquids, or a solid and a liquid can be separated by shaking in a separating funnel (Fig. 8) with a solvent which dissolves either. For example, a mixture

of chloroform and alcohol can be separated with water which is immiscible with chloroform but mixes in all proportions with alcohol. The alcohol distributes itself between water and chloroform, the latter occupies the bottom layer. Chloroform is removed through the stop-cock. The process is repeated with fresh water. The alcohol can thus be removed. Chloroform is then dehydrated with calcium chloride and obtained pure. By fractional distillation, alcohol may be recovered. Ether is commonly used for isolating many organic compounds from their aqueous solutions. Most organic compounds dissolve more freely in organic solvents than in water. Sometimes emulsions are formed during such extraction with solvents. These may be broken by adding an electrolyte, warming or adding more solvent.

Chemical methods.—A compound may also be purified by forming a suitable derivative with another compound. The derivative is decomposed to get back the original compound in pure state. For example, an aldehyde is converted into solid bisulphite compound with sodium bisulphite and filtered. This is then decomposed to obtain the aldehyde. An organic acid may be obtained pure by forming an insoluble metallic salt and decomposing the latter with a mineral acid.

In many cases of purification, often in the last stage (before crystallisation or distillation), the substance in solution is treated with a little animal or active charcoal for decolorisation and in some cases, de-odorisation. The mixture is generally boiled for 5-10 minutes and filtered hot.

Chromatographic methods.—By adsorption or partition chromatography, many organic compounds occurring in minute traces and having similar physical properties, can be completely separated, purified and also identified. The method is based on either selective adsorption of the components by a suitable adsorbent such as alumina, magnesia, calcium carbonate, charcoal, etc. placed in a vertical glass tube, or partition coefficients of the dissolved compounds between two phases—mobile (a mixture of organic solvents, partially soluble in water) and stationary (silica gel or cellulose column, containing hygroscopic moisture, i.e. bound water). In the first method, a solvent is added at the top of the alumina column, then a solution of the mixture and finally, more of the solvent. The components pass down the column at different rates and form separate coloured bands if they are coloured. These are removed and different components extracted with a solvent. In the second case, the mobile phase solvent with the solute, coming from the cellulose column, is collected in a large number of test tubes placed in a fraction collector at regular intervals; these fractions are then examined for individual components.

In **paper chromatography**, a drop of the solution of a mixture is placed at one end of a filter paper strip which dips into a trough of solvent. The solvent front moves due to capillary forces. The other end of the paper hangs downward, the flow of solvent continues then by a syphoning action. The components move with the solvent but at different rates, their respective positions are found with suitable reagents giving coloured products. They may also be separated in pure form from these spots by extraction with solvents, and estimated by micro methods.



Fig. 8. Separating funnel.

Criteria of purity.—The criterion of purity of an organic solid is its *sharp* melting point (some, however, decompose before melting). Most organic solids melt at comparatively low temperatures (below 300°) and very sharply (within 1°) at a definite temperature. An impure sample usually melts through a range of several degrees. Even traces of impurity depress the melting point considerably. An impure sample is purified, say by crystallisation from a suitable solvent, repeatedly and its melting point noted each time. The melting point rises gradually until it is constant and sharp. If a compound melts at the same temperature after recrystallisation, it is generally considered pure. Determination of melting point helps the identification of organic compounds. A eutectic mixture of two or more compounds also has a sharp melting point; but the chance of a mixture to have components in just the proportion required for a eutectic mixture, is rather remote.

Determination of melting point.—For this, an organic solid is finely powdered and thoroughly dried in a desiccator. A little of it is taken in a small capillary tube, about 2 inches long, sealed at one end. The tube is attached to a thermometer (to which it sticks if the latter is wetted with a liquid) so that the solid lies close to the bulb of the thermometer. The thermometer is introduced through a cork into a small Jena glass flask, containing concentrated sulphuric acid (Fig. 9). Sometimes glycerol, high-boiling liquid paraffin, or castor oil is used instead.

The bulb of the thermometer and about a half of the capillary tube are under the liquid surface. The flask is heated by a small, non-luminous flame slowly and cautiously. At a certain temperature the solid, if pure, melts suddenly. This is noted. Near about the melting point, the flame is either removed away or kept low, so that rise in temperature is very slow. The operation may be repeated; the difference should not be greater than 1° . A correction for the mercury column above the liquid (stem correction) may be applied.

If a compound melts with decomposition, it has to be purified by repeated crystallisation; by microscopic examination its purity may possibly be ascertained.

Determination of *mixed melting point* is helpful in the identification of organic compounds. Suppose, the solid under examination is believed to be urea which melts at 132° . This is thoroughly mixed with a little pure urea. If the mixture also melts sharply at 132° , the unknown compound is urea. Otherwise the melting point (m.p.) of the mixture will be indefinite, and lower than 132° . This lowering of m.p. of a compound by an impurity is generally but not universally true; in certain cases there is no depression of m.p. when two different compounds

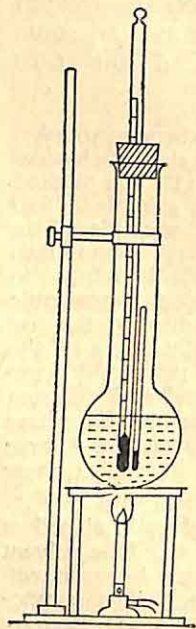


Fig. 9. Determination of melting point.

are mixed together while in others such mixtures melt above the m.p. of either component. These exceptional cases are, however, very rare.

The criterion of purity of an organic liquid is its *sharp* boiling point (b.p.) which is constant provided the barometric pressure does not fluctuate. If the liquid does not decompose at the boiling point, it is subjected to distillation from a distilling flask fitted with a standardised thermometer and a condenser (Fig. 4). If the liquid is pure, the distillation will continue at a constant and definite temperature (within a range of about 1°), and redistillation produces no change in its boiling point. In case it distils with decomposition, the liquid may be distilled under a definite reduced pressure. During the determination of boiling point, overheating or bumping of the liquid must be avoided. Constant-boiling mixtures, as already mentioned, have also sharp boiling points. If such a mixture is distilled under two different pressures, the composition of the distillates is found to be different. Besides the determination of boiling point, other physical constants of liquids such as specific gravity, refractive index, molecular rotation (to be discussed later), etc., are also determined to be certain about the purity of a sample.

QUESTIONS

1. Write a brief essay on the various methods used for purifying organic compounds.
 2. What are the criteria by which the purity of an organic compound may be established?
 3. How would you proceed to separate a mixture of
 - (i) alcohol (b.p. 78°) and acetone (b.p. 56°)
 - (ii) alcohol and chloroform?
 4. Discuss carefully the principle involved in
 - (i) steam-distillation
 - (ii) distillation with a fractionating column.
 5. Write an account of the various methods by which organic compounds are purified. (B.A. Degree Exam., 1942, Madras Uni.).
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CHAPTER II

QUALITATIVE AND QUANTITATIVE ANALYSIS

The first step in arriving at the molecular formula of a compound is to ascertain the constituent elements and their proportion. The elements commonly found in organic compounds are carbon, hydrogen, oxygen, nitrogen, halogens, sulphur, phosphorus and metals; the last four occur less frequently. Qualitative analysis (or detection of elements) is carried out as follows.

Detection of carbon and hydrogen.—Carbon is tested for only when a compound is not definitely known to be organic. Many organic substances burn with a sooty flame, or char when strongly heated in a porcelain crucible, showing the presence of carbon. Some liberate free carbon on addition of concentrated sulphuric acid. The surest way of detecting carbon is by oxidising the substance with copper oxide to carbon dioxide at high temperature. In a hard glass test-tube is taken a little of the dried substance thoroughly mixed with about twenty times of its weight of freshly ignited fine copper oxide. Sufficient copper oxide is added to cover the mixture in the test-tube, fitted with a cork and a delivery tube (Fig. 10). It is then strongly heated; carbon is thus oxidised to carbon dioxide, and hydrogen to water. The water vapour condenses in drops in the cooler parts of the test-tube, and may be confirmed by adding anhydrous copper sulphate which turns blue. The end of the delivery tube leads into a test-tube containing lime-water which turns milky with carbon dioxide. If the compound be a volatile liquid or a gas, the vapour of the liquid or the gas itself is passed through a red-hot glass tube containing coarse, ignited copper oxide. The outcoming gas is tested for

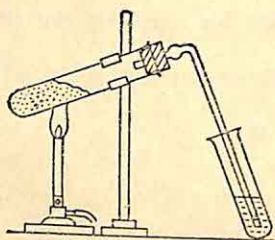


Fig. 10. Detection of carbon and hydrogen.

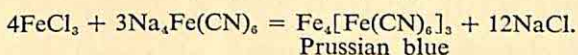
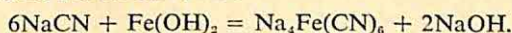
water and carbon dioxide as usual.

Detection of oxygen.—There is no simple method for this. In some cases when the dry anhydrous substance is heated alone in a test-tube, water collects in the cooler parts of the tube, indirectly proving the presence of oxygen. The existence of oxygen-bearing groups such as $-\text{OH}$, $-\text{NO}_2$, $=\text{C}=\text{O}$, etc., in a compound also proves its presence. Oxygen may be detected as carbon dioxide (which turns lime-water milky) formed when the vapour of a compound containing oxygen is passed over hot carbon in an oxygen-free atmosphere.

Detection of nitrogen.—Some organic compounds having nitrogen produce, on heating, an unpleasant smell like that of burnt hair. All nitrogenous compounds respond to the Lassaigne's test which is carried out as follows:

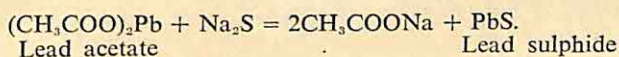
A pea-size piece of clean sodium (or potassium) is taken in an ignition tube and a little (about 0.1 g.) of the substance is added to it. The tube is then gradually heated to redness; if the reaction is violent, it should be removed from the flame, the reaction goes on by itself. A very volatile substance is slowly added to molten sodium. The tube is heated until action ceases. A black, carbonised mass is thus obtained. The hot tube, held at arm's length, is plunged into water (about 20 c.c.) taken in a clean porcelain mortar; the tube crumbles to pieces and the excess of sodium catches fire with water. The hard mass, if any, is powdered and the solution is filtered. To the filtrate is added freshly prepared solution of ferrous sulphate and the mixture boiled for a while. The solution is then acidified with dilute HCl, and one or two drops of ferric chloride solution added. A deep blue coloration or ppt. (Prussian blue) indicates nitrogen.

During fusion, nitrogen of the compound combines with its carbon and sodium added, giving sodium cyanide; this on boiling with ferrous hydroxide (produced from ferrous sulphate and caustic soda) forms sodium ferrocyanide. With ferric chloride, acidified solution of ferrocyanide yields Prussian blue:



Detection of sulphur.—The substance is fused with sodium as in the case of nitrogen. Sulphur in the compound forms sodium sulphide. The filtered, alkaline solution is tested with either

- (i) a drop of freshly prepared, dilute solution of sodium nitro-prusside, sodium sulphide gives a violet coloration ; or
(ii) acetic acid and lead acetate solution, a black ppt. of lead sulphide confirms sulphur.



Sulphur and nitrogen can be detected simultaneously by adding a few drops of ferric chloride to the filtrate from sodium fusion acidified with hydrochloric acid. A blood-red colour indicates thiocyanate and hence the presence of both sulphur and nitrogen.

Detection of halogens.—Halogens in organic compounds cannot usually be tested with silver nitrate as they do not ionise in solution, most of them are insoluble in water. The compound is fused with metallic sodium as before. The halogens form sodium halides. The filtered aqueous extract of the fused mass is boiled with an excess of dilute HNO_3 to drive off H_2S and HCN which are formed if sulphur and nitrogen are also present. The solution is cooled and AgNO_3 solution added—a curdy, white or yellow ppt. indicates halogen. The silver halide is identified as usual.

In a recent modification, sodium carbonate and sugar, or sodium carbonate and zinc dust are conveniently used instead of sodium.

A halogen may also be detected by fusing the mass with quicklime in a small crucible. The residue is extracted with water and filtered. Calcium halide formed remains in the filtrate and is identified with AgNO_3 solution in the same way. *Beilstein's test* for halo-

gens consists in heating the substance on a copper oxide wire in a Bunsen flame which is coloured green. The presence of nitrogen does not usually interfere. The test is very sensitive but a few compounds containing no halogen, *e.g.*, urea, also give it.

Detection of phosphorus.—It is detected by fusing the compound with sodium carbonate and potassium nitrate—when alkali phosphate is formed. The fused mass is boiled with water and filtered. The filtrate is acidified with conc. HNO_3 and an excess of ammonium molybdate solution added; a heavy, yellow ppt. confirms phosphorus.

Arsenic, if present, is converted to an arsenate by this process, and detected as usual.

Detection of metals.—This is done by first igniting the substance on a platinum foil, or in an open porcelain crucible. Oxides or carbonates of metals are thus obtained, which are identified by ordinary analytical methods. Volatile metals like arsenic or mercury may be detected in the residue obtained by oxidising the compound with a mixture of strong HNO_3 and H_2SO_4 .

Estimation of carbon and hydrogen.—All organic compounds are completely oxidised by red-hot cupric oxide; carbon forms carbon dioxide, and hydrogen water. Carbon and hydrogen are invariably determined in one operation. CO_2 and H_2O from a known weight of the substance are absorbed by suitable arrangements and weighed. The method, mainly due to Liebig (1831), is employed even to-day with slight modification.



Fig. 11a. Combustion tube.

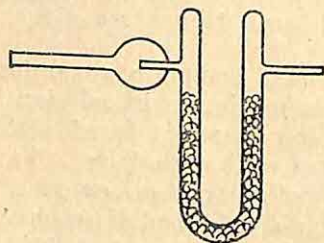


Fig. 11b. Calcium chloride U-tube.

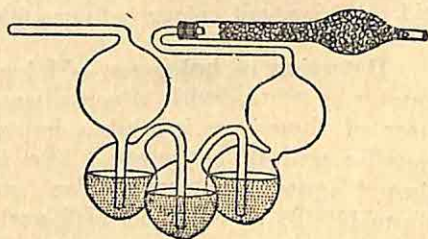


Fig. 11c. Potash bulbs.

The apparatus consists of a hard glass combustion tube (Fig. 11a) about 90 cm. in length and 12-15 mm. in diameter. Nearly two-thirds (pp') of the tube are filled with coarse copper oxide, kept in position by loose asbestos plugs. Before starting the experiment, the tube is strongly heated in the furnace (Fig. 11d) consisting of a row of burners and closed by a set of fire-clay tiles. Air, completely freed from CO_2 and moisture by passing through conc. H_2SO_4 in a gas-washer and soda-

lime in U-tubes, is led through the tube. The inside of the combustion tube and its contents are thus thoroughly dried and also freed from carbon dioxide and organic matter, if any. The tube is cooled and its free end connected through a rubber cork to an accurately weighed U-tube (Fig. 11b) containing granulated (not fused) and sieved calcium chloride. The other end of the U-tube is joined by means of a short, thick rubber tubing to a weighed potash bulb (Fig. 11c), containing a 50% aqueous solution of KOH. The free end of the potash bulb carries a small tube half-filled with soda-lime. This serves as a guard against the diffusion of acidic or aqueous vapours from outside. *All connections must be perfectly air-tight.*

About 0.2 g. of the substance, powdered and dried, is weighed into a small porcelain boat (C). This is introduced into the combustion tube. A spiral roll of copper gauze (B), previously coated with copper oxide by heating strongly in a non-luminous Bunsen flame, is then placed behind the boat to prevent the backward diffusion of the products of combustion. Before heating, a slow current of air (and towards the end, oxygen) is passed through the combustion tube as before. The tube is then gradually heated from both ends, proceeding slowly towards the boat. The air- or oxygen-flow through the tube is regulated at 2-3 bubbles per second. The heating is continued until nothing is left on the boat. This normally takes about 2 hours. The apparatus is cooled to the room temperature. The potash bulb and the calcium chloride tube are disconnected, stoppered and weighed. Cupric oxide oxidises the compound; air brings the vapour of the compound in contact with cupric oxide, maintained at 600° – 800° .

Calculation :

Let w = weight of the substance taken,

w_1 = increase in the weight of the potash bulb,

and w_2 = increase in the weight of the calcium chloride tube.

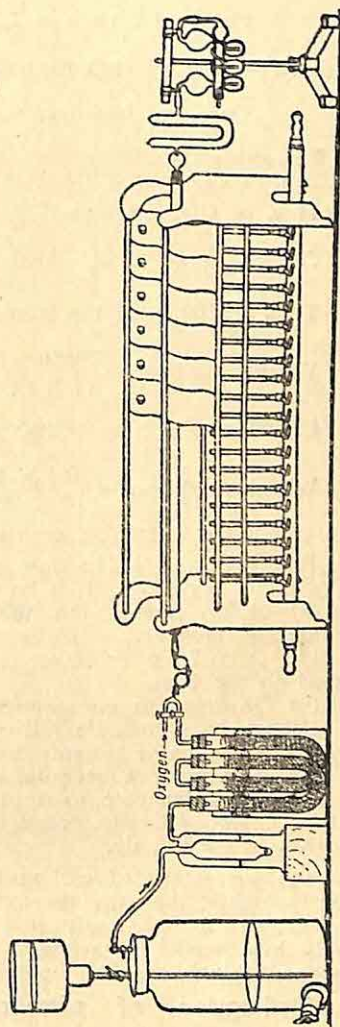


Fig. 11d. Combustion apparatus for estimation of carbon and hydrogen.

Therefore, weight of CO_2 produced = w_1 g.

$$\text{Or \% of carbon} = \frac{12 \times w_1}{44} \times \frac{100}{w} = \frac{300w_1}{11w}$$

Similarly, weight of H_2O formed = w_2 g.

$$\text{Or \% of hydrogen} = \frac{2 \times w_2}{18} \times \frac{100}{w} = \frac{100w_2}{9w}$$

Example : 0.3560 g. of an organic compound gave on combustion 1.2220 g. of CO_2 and 0.200 g. H_2O . What is its percentage composition ?

44 g. of CO_2 contains 12 g. of carbon.

$$\therefore 1.2220 \text{ g. of } \text{CO}_2 \text{ has } \frac{12}{44} \times 1.2220 \text{ or } \frac{3.6660}{11} \text{ g. of carbon.}$$

Thus 0.3560 g. of the substance contains $\frac{3.6660}{11}$ g. of carbon.

$$\text{Whence carbon} = \frac{3.6660 \times 100}{11 \times 0.3560} \text{ or } 93.62\%.$$

0.3560 g. of it gave 0.2000 g. of water, i.e., $\frac{0.2 \times 2}{18}$ g. of hydrogen.

$$\text{Whence hydrogen} = \frac{0.4 \times 100}{18 \times 0.3560} \text{ or } 6.24\%.$$

The compound, therefore, contains no other element.

Precautions.—(1) The flow of oxygen through the combustion tube should be carefully regulated. If it be too rapid, carbon monoxide will be formed.

(2) Before combustion, the tube must be completely freed from carbon dioxide and moisture.

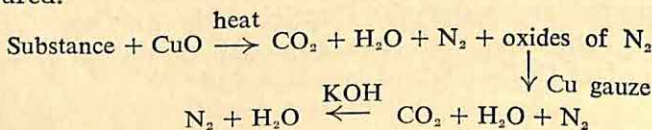
(3) A volatile substance should be weighed in a small bulb which is placed on the boat.

(4) Nitrogenous compounds form oxides of nitrogen which are reduced to nitrogen by a metallic roll of copper gauze placed in the combustion tube, beyond copper oxide towards the U-tube so that they cannot vitiate the results.

(5) For halogen or sulphur compounds, coarse copper oxide is replaced by fused lead chromate, to form halide or sulphate of lead—no halogen or SO_2 is thus absorbed by the potash bulb. If only halogen be present, a bright roll of silver gauze will do.

The percentage of carbon is generally a bit lower, and that of hydrogen slightly higher, than the theoretical values. This is because dry air or oxygen carries away a little moisture from the potash bulb, and copper oxide, being highly hygroscopic, tenaciously retains a little moisture even after preliminary roasting; this is expelled on prolonged heating afterwards.

Estimation of nitrogen by Dumas' method.—All organic nitrogenous compounds completely decompose into carbon dioxide, water and nitrogen (or its oxides to some extent) on strongly heating with copper oxide. These are passed over a heated copper gauze to reduce oxides of nitrogen and finally collected over caustic potash which retains the carbon dioxide. The volume of nitrogen collected is measured.



A combustion tube similar to that for estimating carbon and hydrogen is employed (Fig. 12). The portion AB is filled with coarse copper oxide, the two ends of the oxide layer are plugged with asbestos.

The weighed substance (about 0.3 g.) is intimately mixed with about 10 g. of fine copper oxide (ignited and cooled) and carefully introduced through a small, dry funnel into the combustion tube (column BC in Fig. 12). Another column of coarse copper oxide (CD) is introduced. A bright spiral of copper gauze (E), freshly reduced in methyl alcohol vapour, is placed at the end of the tube which is connected to a Schiff's nitrometer (N), filled with 40% aqueous KOH solution. The other end is connected to a supply of carbon dioxide generated by heating NaHCO_3 (or magnesite) in a hard glass tube closed at one end. Between this and the combustion tube, there is a gas-washer containing conc. H_2SO_4 for arresting the water vapour and also for noting the rate of flow of CO_2 . The combustion tube is placed in the furnace and to begin with, the bicarbonate is gently heated; the CO_2 evolved sweeps out the air in the tube. After some time, the nitrometer is connected to the combustion tube and more CO_2 passed. This bubbles up the KOH column and is completely absorbed. Any air collects at the top of the nitrometer. When no gas accumulates in ten minutes, heating is started from the two ends of the furnace; as the copper gauze and the coarse oxide become dull red, the substance is heated carefully so that not more than one bubble per second escapes into the nitrometer. A slow stream of CO_2 is passed through the combustion tube all the while. When no more nitrogen collects in the nitrometer,

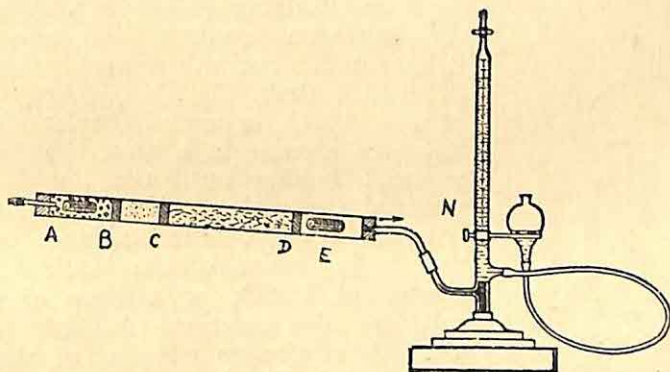


Fig. 12. Estimation of nitrogen by Dumas' method.

the combustion is complete (this takes about 30 minutes); a strong stream of CO_2 sweeps out the residual nitrogen. The apparatus is then cooled to the room temperature and the volume of nitrogen measured after making the level inside and outside the same. The room temperature and barometric pressure are noted.

Calculation :

Let v_1 = volume of nitrogen collected,

$t^\circ\text{C}$ = temperature of the room,

P = barometric pressure,

p = aqueous tension at $t^\circ\text{C}$,

v_2 = volume the gas would occupy at N.T.P.

$$\text{then, } v_2 = \frac{v_1 \times (P-p) \times 273}{(273 + t) \times 760}$$

If w g. be the weight of the substance, w g. contains $\frac{v_2 \times 28}{22400}$ g. of nitrogen.
 ($\therefore$ 22.4 litres at N.T.P. weigh 28 g.)

$$\therefore \% \text{ of } N_2 = \frac{v_2 \times 28}{22400} \times \frac{100}{w} = \frac{v_2}{8w} = \frac{v_1 \times (P-p) \times 273}{8 \times w \times 760 \times (273 + t)}$$

The value for nitrogen is usually about 0.2% too high due to a little air retained by copper oxide. If the combustion is incomplete, any carbon monoxide or methane formed escapes oxidation and counts as nitrogen.

Kjeldahl's method.—Most organic nitrogenous compounds form ammonium sulphate quantitatively on heating with conc. H_2SO_4 , which on distilling with caustic soda, gives ammonia. This is absorbed by a known volume of standard acid and determined by titration. The method is convenient and generally used in agricultural and biological laboratories as unlike Dumas', several estimations can be simultaneously done.

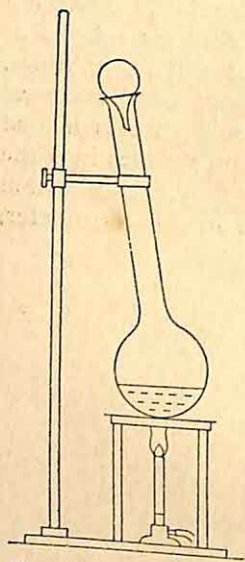


Fig. 13a. Kjeldahl's flask.

The substance (0.5 to 5 g. according to the nitrogen content) is taken in a long-necked, round-bottomed Pyrex flask (Kjeldahl's flask, Fig. 13a). About 20 c.c. of conc. H_2SO_4 is poured upon it. The flask is heated directly in a fume chamber slowly to mild boiling until the liquid becomes practically colourless. About 10 g. of K_2SO_4 is added to effect better oxidation by raising the boiling point of the liquid. A small crystal of $CuSO_4$ or a drop of mercury catalyses the reaction. A little selenium (0.1 g.) accelerates clearing of the liquid. The cooled liquid, diluted carefully with

water, is transferred to a round-bottomed, hard glass litre-flask for distillation (Fig. 13b).

Excess of a 40% caustic soda solution (80 c.c. for 20 c.c. acid) is added *without* mixing with the acid. Some pumice stone or zinc granules prevent bumping. The lower end of an upright condenser dips into a conical flask containing a known volume of decinormal H_2SO_4 and a few drops of methyl orange. The upper end of the condenser is connected to the distillation flask through a trap which prevents the splashing of any alkaline solution from the flask to the condenser. The liquid is slowly heated to avoid too rapid evolution of ammonia, it is then boiled until the distillate is no longer alkaline. The acid in the conical flask is titrated to determine the

ammonia. A blank experiment is performed under identical conditions and a correction made accordingly.

If v c.c. of normal acid is consumed, $\frac{v}{1000}$ equivalents of ammonia have been evolved, which mean $\frac{v \times 14}{1000}$ g. of nitrogen.

$\therefore$ % of nitrogen = $\frac{v \times 14}{1000} \times \frac{100}{w} = \frac{1.4v}{w}$, w being the weight of substance.

In pyridine, quinoline, azo-, diazo-, nitro-compounds, etc., nitrogen is present in a non-oxidisable form. This method is not applicable to them. Some compounds give low values due to evolution of nitrogen during digestion.

Estimation of halogens by Carius' method.—The substance is oxidised with fuming HNO_3 at high temperature in presence of silver nitrate. From the amount of silver halide formed, the halogen is calculated.

Into a thick-walled Jena glass tube (about 50 cm. long and 2 cm. in diameter) sealed at one end (Carius tube) are introduced through a thistle funnel about 3 c.c. of fuming HNO_3 (sp. gr. 1.5) and some crystals of AgNO_3 . The substance (0.15 to 0.2 g.) weighed in a small glass tube is slipped down the Carius tube which is then sealed, leaving a nose. It is heated gradually up to 200° – 250° for about four hours in a bomb furnace.

This consists of iron jackets to hold the glass tubes, and an iron or wooden enclosure with a door of thick glass to guard against explosion. The temperature is noted by a thermometer inserted in the furnace and heating is done by Bunsen burners (Fig. 14). Finally, the tube is cooled and the pressure inside released by softening the nose or projected end with a flame. The tube is cut open and the contents diluted with water and transferred to a beaker. The silver halide is boiled with water, collected in a Gooch crucible

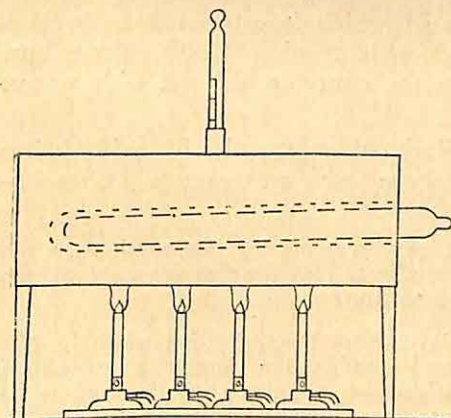


Fig. 14. Carius' estimation of halogens.

or sintered glass filter, washed, dried and weighed.

If w_1 g. of the substance yields w_2 g. of silver chloride (say), it contains $\frac{w_2 \times 35.5}{108 + 35.5}$ g. of chlorine, whence chlorine = $\frac{35.5 \times w_2}{143.5} \times \frac{100}{w_1}$ %.

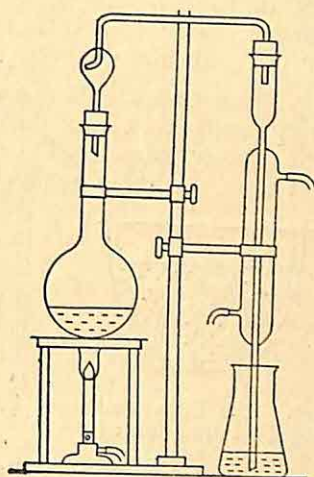


Fig. 13b. Kjeldahl's estimation of nitrogen.

This method is suitable for determining halogens in volatile organic compounds; but accurate results are seldom obtained in case of highly halogenated aromatic substances. Iodine compounds generally give low values as AgI produced is appreciably soluble in HNO_3 containing AgNO_3 .

Piria and Schiff's method may be employed for some halogen compounds that are incompletely decomposed in Carius' method. The finely powdered substance (0.1-0.3 g.) is taken in a small platinum crucible which is completely filled up with an intimate mixture of pure lime and sodium carbonate (4: 1). A larger platinum or porcelain crucible is inverted over it and the whole system inverted once again. The space between the two is filled, and the smaller crucible completely covered, with the same mixture (Fig. 15). It is heated first with a Bunsen flame and then more strongly with a blow-pipe burner. It is cooled, the contents are treated with water and dissolved in dilute nitric acid. The solution is

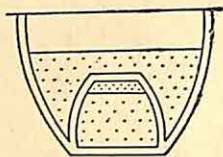


Fig. 15. Piria and Schiff's estimation of halogens.

filtered and the halogen precipitated with AgNO_3 solution. From the weight of silver halide, halogen is calculated as in Carius' method. For iodine compounds sodium carbonate alone is used as calcium iodate which results if lime is employed, is insoluble in water.

In **Robertson's method** the substance is boiled with a powerful oxidising agent, such as chromic acid, in a current of purified air. The vapours are led over finely divided platinum, kept red-hot in a quartz or silica tube, the halogens (chlorine and bromine) are thus set free. The latter is absorbed in alkaline hydrogen peroxide and estimated volumetrically. This method is well suited for volatile compounds.

Estimation of sulphur.—In Carius' method, sulphur in an organic compound is oxidised to sulphuric acid which is estimated as barium sulphate. The compound is heated with fuming HNO_3 alone and barium chloride solution is added to the contents, diluted with water, before boiling.

Phosphorus is determined similarly, the phosphoric acid being weighed as magnesium pyrophosphate or ammonium phosphomolybdate as usual.

Estimation of oxygen.—There is no easy method for determining oxygen in organic compounds. The usual procedure is to find the percentage of oxygen by difference, those for other elements being known.

In **Ter Meulen's method**, oxygen is estimated by heating strongly the substance in a current of hydrogen and passing the vapour over red-hot 350° . The oxygen is thus converted into water which is absorbed by CaCl_2 as usual and weighed.

Micro-analysis, elaborated by Pregl, requires only 3 to 5 mg. of a substance for each determination. The basic principle is the same as described above but the apparatus is specially adapted and weighing done in a micro-balance having a sensitivity of 0.001 mg. In semi-micro method, 20-25 mg. is taken for each estimation. These have proved extremely helpful in the study of many natural products which occur in traces and only a few mg. of which can

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be obtained in pure state; ordinary macro methods require about 0.1–0.5 g. of the material for such estimations, depending on the element.

QUESTIONS

1. How would you detect the presence of the following elements in organic compounds: (i) nitrogen (ii) sulphur (iii) halogens? Discuss the principle involved in each case.

2. Describe in detail the Carius' method of estimating halogens.

3. Discuss the important methods employed for determining the percentage of nitrogen in organic compounds. Which method would you prefer for routine analysis?

4. Describe the process of combustion of an organic compound; and mention the special precaution to be adopted when the substance is very volatile.

5. Calculate the percentage of nitrogen from the following data: 0.5 g. of the substance was decomposed and distilled with caustic soda and the ammonia collected in 50 c.c. of normal sulphuric acid. The excess acid required 33.6 c.c. of normal caustic soda solution for neutralisation.

6. Describe with essential practical details how you would estimate the percentage of nitrogen in an organic compound (Bombay University, B.A. & B.Sc. 1937; B.Sc. Pass, 1945, Calcutta University; B.Sc. Pass 1952, Gauhati Uni.).

7. How would you test for the presence of nitrogen, chlorine and sulphur in an organic compound? How is nitrogen quantitatively determined in a compound containing carbon, hydrogen, oxygen, sulphur and nitrogen? (B.A. Degree Exam., 1941, Madras Uni.).

8. Describe the qualitative test for halogens in organic compounds and the quantitative method for their estimation. In what structural forms are they commonly present? (B.A. Degree Exam., 1946, Madras Uni.).

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CHAPTER III

EMPIRICAL FORMULAE AND MOLECULAR WEIGHTS

From quantitative elementary analysis, the percentage composition of an organic compound is found readily. The relative number of atoms of constituent elements is then calculated from its percentage composition as in the case of inorganic compounds. For this, the percentage weight of each element is divided by its atomic weight. The atomic ratio thus obtained is expressed in whole numbers by dividing, if necessary, each quotient by the lowest one, or by a simple fraction of it. The formula, expressing the atomic ratios of the elements present in the molecule in whole numbers, thus obtained, is known as *empirical formula*. Some illustrations will make it clear.

(i) On analysis, a compound was found to contain C = 83.7% and H = 16.28%. What is its empirical formula?

Dividing the percentage composition by respective at. wts., we have

$$H = \frac{16.28}{1.008} = 16 \text{ approximately}$$

$$C = \frac{83.7}{12.0} = 7 \quad ,$$

The empirical formula is, therefore, C_7H_{16} ; 7 and 16 denote the relative number of carbon and hydrogen atoms in the molecule. The molecular formula is $(C_7H_{16})_n$; n , a whole number, is known from the molecular weight.

(ii) An organic compound contains C = 48.8% and H = 3.1%. Find its empirical formula.

The percentage weights of the elements do not total 100, so oxygen is present; its percentage is obtained by difference.

$$\text{Thus } C = 48.8\%$$

$$H = 3.1\%$$

$$\therefore O = (100 - 48.8 - 3.1) = 48.1\%$$

$$\text{Hence } C = \frac{48.8}{12.0} = 4.07 = 4 \text{ approximately}$$

$$H = \frac{3.1}{1.0} = 3.1 = 3 \quad ,$$

$$O = \frac{48.1}{16} = 3.01 = 3 \quad ,$$

Hence the empirical formula is $C_4H_3O_3$ and the molecular formula $(C_4H_3O_3)_n$.

(iii) On analysis an organic compound was found to contain C = 43.98%, Cl = 37.18%, H = 2.09%. Calculate the empirical formula (B.Sc. Lond. 1925).

$$C = 43.98\%$$

$$H = 2.09\%$$

$$Cl = \frac{37.18\%}{83.25\%} \quad \therefore O = (100 - 83.25) = 16.75\%.$$

The relative numbers of the atoms are :

$$C = \frac{43.98}{12.0} = 3.66$$

$$H = \frac{2.09}{1.0} = 2.09$$

$$Cl = \frac{37.18}{35.5} = 1.05$$

$$O = \frac{16.75}{16} = 1.04$$

Dividing each by $\frac{1.04}{2}$ we have, to the nearest accuracy, the empirical formula as $C_7H_4O_2Cl_2$.

Due to unavoidable experimental errors, exact theoretical values are seldom obtained from analysis. Two compounds may have very nearly the same percentage composition, *e.g.*, C_3H_7 has $C = 83.72\%$; $H = 16.28\%$; and C_7H_{16} has $C = 84\%$, $H = 16\%$. So also $C_{20}H_{42}$ and $C_{30}H_{62}$. Without other data, *e.g.*, mol. wt., it is hardly possible to arrive at the correct formula in such cases. Several organic compounds may have the same empirical formula, their molecular formula may or may not be different. Thus formaldehyde, acetic acid, lactic acid and glucose have the same empirical formula, CH_2O , but different molecular formulae, *viz.*, CH_2O , $C_2H_4O_2$, $C_3H_6O_3$ and $C_6H_{12}O_6$ respectively. Glucose, fructose and galactose have the same empirical formula, CH_2O , and also the same molecular formula, $C_6H_{12}O_6$.

Determination of molecular weight is best done by physical methods depending upon the nature of the substance. Molecular weights of volatile organic solids and liquids are found by vapour density method of Victor Meyer, Hofmann or Dumas. This is based upon the fact that the relative density of a gas or vapour is half its molecular weight (derived from Avogadro's hypothesis). One has to find the volume that a given weight of the substance occupies as vapour under definite temperature and pressure.

Victor Meyer's method.—The apparatus of Victor Meyer consists of an elongated glass bulb with a long, narrow stem and a bent capillary side-tube. This is introduced into a copper jacket containing a liquid which boils at least 25° higher than the substance to be examined. The end of the long stem is tightly closed with a rubber stopper; the side-tube leads to a graduated tube filled with water and inverted over a trough of water (Fig. 16).

The Victor Meyer tube, thoroughly cleaned and dried, is kept in position in the copper jacket with a well-fit cork. There is an outlet for the vapour of the heating liquid. The liquid in the

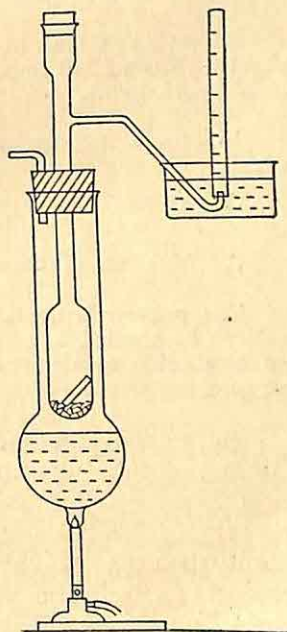


Fig. 16. Victor Meyer's apparatus.

copper vessel is kept boiling. The air inside the Victor Meyer tube expands and goes off. When the bulb attains a uniform temperature and no air bubbles out, the graduated tube, completely filled with water, is inverted over the end of the side-tube. A small glass-stoppered bottle or a thin-walled glass tube sealed at both ends containing a known weight of the substance is swiftly dropped into the tube by opening the rubber stopper which is *immediately* replaced. The bulb has a pad of asbestos or glass wool to absorb the shock. Before introduction, the seal may be broken. Immediate vaporisation takes place and the displaced air, equal to the volume the compound occupies as vapour, collects in the graduated tube. When no more bubbles issue out, it is transferred to a tall jar of water to attain room temperature. The volume of the gas is then measured after making the level of water inside and out the same. The barometric pressure and temperature are noted.

Let V_1 = the observed volume at $t_1^\circ\text{C}$ under a pressure, P_1 cm.

Let p cm. be the aqueous tension at t_1° . Then V , the volume of the displaced air at N.T.P. = $\frac{(P_1 - p) \times V_1}{(273 + t_1)} \times \frac{273}{76}$ c.c.

Vapour density = $\frac{W}{V \times '00009}$, W being the wt. of the compound.

$$\therefore \text{Mol. wt.} = \frac{2 \times W}{V \times '00009} = \frac{2 \times W \times 76 \times (273 + t_1)}{0'00009 \times V_1 \times (P_1 - p) \times 273}$$

Example: 0.1680 g. of a substance, when vaporised, displaced 49.4 c.c. of air at 20°C and 740 mm. pressure. Calculate its molecular weight (aq. tension at $20^\circ = 18$ mm.).

$$\text{Volume of vapour at N.T.P.} = \frac{49.4 \times (740 - 18) \times 273}{293 \times 760} \text{ c.c.}$$

$$\therefore \text{Vapour density} = \frac{0.1680 \times 293 \times 760}{49.4 \times 722 \times 273 \times 0'00009}$$

$$\therefore \text{Mol. wt. of the compound} = \frac{2 \times 0.1680 \times 293 \times 760}{49.4 \times 722 \times 273 \times 0'00009} = 85.39.$$

Victor Meyer's method is extensively employed as it gives accurate results and can be applied to compounds having a wide range of b.p. It is of course not applicable to compounds which boil with decomposition at atmospheric pressure.

Hofmann's method.—The apparatus consists of a graduated barometer tube of about 2 cm. in diameter and nearly 90 cm. in length. It is filled with mercury and inverted over a trough of mercury. The tube is almost completely surrounded by an outer jacket through which vapour from a boiler is passed. When the temperature of the barometer tube is steady, a small stoppered bottle, completely filled with a liquid of known weight (about 0.05 g.), is introduced at the bottom of the tube. The bottle immediately rises to the top of the mercury and the liquid vaporises instantaneously in the Torricelli's space. The level of mercury is depressed, and when it becomes stationary, the volume of the vapour is noted

and also the temperature. The pressure of the vapour is obtained by subtracting the reading of the mercury level from the barometric reading. The weight of the vapour being known, the vapour density is calculated as in the previous case. This method is particularly suitable for compounds which decompose at the boiling point under normal pressure. Here vaporisation takes place under much reduced pressure and decomposition is avoided.

Dumas' method.—In contrast with the above methods, here the weight of a known volume of vapour at a definite temperature and pressure is determined, from which the relative density is calculated. It gives accurate results but the procedure is troublesome.

A large glass bulb with a narrow, pointed neck is weighed. A few c.c. of the liquid is introduced into it by alternate heating and cooling. The bulb is kept immersed in a bath whose temperature is appreciably higher than the boiling point of the liquid. The liquid boils rapidly and fills up the bulb with vapour. When no vapour issues out, the orifice is sealed with a blow pipe. The bulb is taken out, cooled, washed thoroughly, dried and weighed. The volume of the bulb is determined by opening the seal under water (when water fills the bulb) and weighing it with water. Knowing the weight and volume of the vapour, its density is readily obtained. For non-volatile substances, cryoscopic (or freezing point) method and ebullioscopic (or boiling point) method are generally employed.

Cryoscopic method is based on the fact that when different substances (non-electrolytes) are dissolved in a solvent in the same molecular concentration, the freezing point of the solvent is lowered to the *same* extent, provided the solution is dilute. Such lowering is directly proportional to the concentration of the solute within certain limits and independent of its nature. Thus 3.42 g. of cane-sugar (mol. wt. 342) and 0.60 g. of urea (mol. wt. 60), dissolved separately in 100 g. of water, lower the freezing point of water to the same extent.

The depression of freezing point of a solvent caused by the gram molecular weight (M) of any non-electrolyte dissolved in 100 g. of the solvent is, therefore, the same. This is called *molecular depression* and usually denoted by C. The value of C varies with solvents and is determined by dissolving a definite weight of a substance of known molecular weight in 100 g. of the solvent and noting the depression. The molecular depression for water is 18.8; i.e., if one gram molecule of any non-electrolyte (60 g. of urea, or 342 g. of cane-sugar, for example) be dissolved in 100 g. of water, the freezing point of the solution should be -18.8° (pure water freezing at 0°). C can also be derived from van't Hoff's equation, $C = \frac{0.02T^2}{L}$, where T is the freezing point of the solvent on the absolute scale and L its latent heat of fusion per gram.

If 1 g. of a substance be dissolved in 100 g. of a solvent whose depression constant is C , the depression in freezing point $d = \frac{C}{M}$, where M = mol. wt. of the solute. Again, if w g. be dissolved in W g. of solvent,

$$d = \frac{C}{M} \times \frac{w \times 100}{W} \text{ or, } M = \frac{C \times w \times 100}{d \times W}.$$

The apparatus (Fig. 17), due to Beckmann, consists of a large glass tube, about 2.5 cm. in diameter, having a side-tube. The tube is closed with a rubber stopper through which passes a Beckmann thermometer; the side-tube is also closed likewise. It is inserted into another empty glass tube serving as an outer air-jacket. The latter is placed in a cold bath at about 5° below the melting point of the solvent. The outer cold bath is stirred with a stirrer by hand, while inside the Beckmann tube, an electrical stirrer operates by a make-and-break arrangement.

The Beckmann thermometer covers a range of 5° - 6° graduated in one-hundredth of a degree. It records not the actual but the difference of temperature (which is required here). The thermometer is highly sensitive, having a large bulb. The amount of mercury in the bulb can be adjusted by transferring a portion to a small reservoir at the top of the thermometer by heating or cooling. The end of the mercury thread must remain on the graduated scale at the freezing temperature of the solvent and solution.

A known weight of the pure solvent is taken in the Beckmann tube and cooled with stirring. The mercury thread of the Beckmann thermometer goes down, sinks below the freezing point of the solvent due to supercooling and then shoots up suddenly and remains stationary at a point which is the freezing point of the solvent. This is noted. The substance (0.2-1.5 g.) is introduced through the side-tube, and the solvent liquefied. The freezing point of the solution is likewise determined. The difference between the two gives the depression; the molecular weight is calculated from the formula given above. Some of the common solvents are:

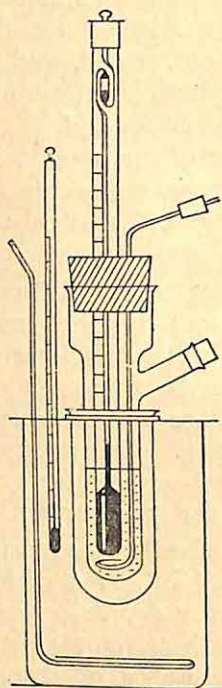


Fig. 17. Freezing-point apparatus (Beckmann).

Solvent		m.p. $^\circ\text{C}$	mol. depression, $^\circ\text{C}$.
Water	...	0	18.8
Phenol	...	42	72
Acetic acid	...	16	39
Benzene	...	5	51
Nitrobenzene	...	5	71
Camphor	...	180	400
Naphthalene	...	80	69

Example : The freezing point of pure benzene is 5.440° and that of a solution containing 2.093 g. of benzaldehyde in 100 g. of benzene is 4.440° . Calculate the molecular weight of benzaldehyde, taking the molecular depression of benzene as 50.

$$2.093 \text{ g. benzaldehyde} = \frac{2.093}{M} \text{ gm. mols., } M \text{ being its mol. wt.}$$

$$\text{Depression of freezing point} = 5.44^{\circ} - 4.44^{\circ} = 1^{\circ}$$

$$1^{\circ} = 50^{\circ} \times \frac{2.093}{M}, \text{ whence } M = 104.6.$$

Molecular depression constant of camphor being very high, viz., 400, a given weight of a solute causes a much greater depression in camphor than in other solvents. An ordinary thermometer can, therefore, be used to determine the m.p. of camphor, which is high, in an ordinary melting point apparatus. The substance, of course, must dissolve freely in molten camphor and must not decompose under the conditions or react with it. The method, called **Rast's method**, is simple and gives accurate results: 5-10 mg. of the substance is thoroughly mixed with 50-100 mg. of pure camphor by melting in a sealed test-tube. The m.p. of the pulverised mixture is determined in the usual way and also that of camphor. Mol. wt. is then obtained from the equation on p. 26.

Ebullioscopic method.—The boiling point of a liquid rises due to dissolved substances. Different substances, in the same molecular

concentration, raise the boiling point of the solvent to the *same* extent. This is independent of the nature of the solute (non-electrolytes). Provided the solution is dilute, the rise in boiling point is directly proportional to the molecular concentration of the solute. The elevation of boiling point caused by the molecular weight in grams of any substance in 100 g. of the solvent is, therefore, the same. This is called *molecular elevation* and denoted by c (cf. cryoscopic method). c being known, the molecular weight of a substance can be calculated by observing the elevation in the boiling point of a definite weight of the solvent by a known weight of the solute, from the formula

$$M = \frac{100 \times c \times w}{d \times W} \text{ where, } d \text{ is the eleva-}$$

tion in the boiling point and other terms have the same significance as in the previous method. Evidently, success of the experiment depends upon the accurate determination of d .

Beckmann's method.—A weighed amount of a pure solvent, say 20 g., is boiled in the tube B (Fig. 18), at the bottom of which a platinum wire is sealed. Sometimes a few glass beads are also introduced. These prevent superheating, the chief source of error, by breaking up the bubbles of vapour. The boiling tube, B, is provided

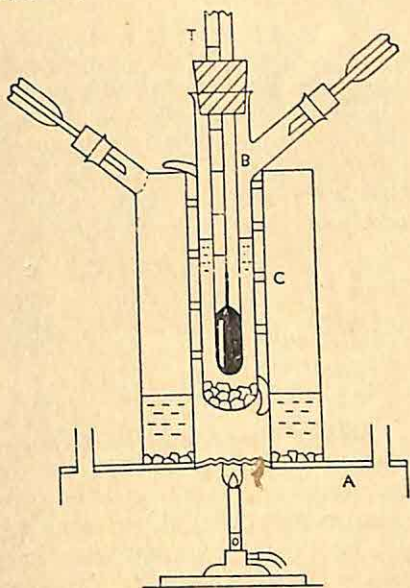


Fig. 18. Beckmann's boiling-point apparatus.

with a coiled air condenser which returns the liquid to the tube as it condenses and keeps the volume of the liquid constant. It is surrounded by a vessel C, in which the same solvent is kept boiling. This, too, has a reflux condenser to avoid loss of the liquid. The apparatus is heated on an asbestos box, A. The boiling tube rests on two asbestos rings and carries a Beckmann thermometer, T, set to the desired range. When the liquid boils briskly, the thermometer is read off. The condenser is removed after cooling the apparatus, and the substance (0.2-1.5 g.) is introduced through the side-tube. The solution is boiled once more, and the boiling point noted. The difference gives d . Heating may also be done electrically.

Example: The molecular elevation for acetone is 16.74° . A solution, containing 0.7269 g. of camphor, dissolved in 32.08 g. of acetone (b.p. 56.30°), boiled at 56.55° . What is the molecular weight of camphor?

The observed elevation = $56.55^\circ - 56.30^\circ = 0.25^\circ$.

$$\text{Wt. of camphor in 100 g. of solvent} = \frac{0.7269}{32.08} \times 100 \text{ g.}$$

$$\text{or } \frac{7269}{3208} \times \frac{1}{M} \text{ gram molecules. } [M = \text{mol. wt. of camphor}]$$

$$\therefore 0.25 = 16.74 \times \frac{7269}{3208 \times M}, \text{ whence } M = 148.4.$$

The method seldom gives accurate results owing to fluctuation in the boiling point due to radiation, change in barometric pressure, mixing of condensed vapour with the boiling liquid, etc. The molecular weights of electrolytes in ionising media as well as of substances that associate and form molecular aggregates, cannot be found by this method. The following are some of the common solvents:

	b.p. $^\circ\text{C}$	c		b.p. $^\circ\text{C}$	c
Water	... 100	5.2	Benzene	... 80.5	26.7
Acetone	... 56	16.7	Acetic acid	... 118	25.3
Chloroform	... 61	36.6	Phenol	... 182	30.4
Methyl alcohol	... 64	9.2	Aniline	... 184	32.2
Ethyl alcohol	... 78	11.5	Ether	... 35	21.1

Mol. wts. of organic acids.—The equivalent weight of an organic acid may be determined by titrating a known weight (0.2-0.5 g.) of the pure acid dissolved in aqueous alcohol with decinormal caustic soda or baryta solution using phenolphthalein as indicator. This can also be found by analysing its silver salt. Generally speaking, silver salts of organic acids are normal, sparingly soluble in water, and crystallise without any water of crystallisation. On ignition, a residue of metallic silver is left. From the weight of silver salt and of silver obtained therefrom, the equivalent weight of the acid is calculated. The molecular weight is obtained from a knowledge of its basicity, for basicity $\times$ equivalent wt. = mol. wt.

The acid is treated with ammonia to obtain the soluble ammonium salt. Excess of ammonia is boiled off and silver nitrate solution added in the cold—the silver salt precipitates. This is filtered, washed and dried. About 0.5 g. of it is ignited in a platinum or porcelain crucible. The difficulty with silver salts is that they are unstable and some of

them explode on ignition. Barium or calcium salts are also employed for this purpose.

Let w_1 g. of silver salt yield w_2 g. of silver, and n be the basicity of the acid. Then, 108 g. of silver would be obtained from $\frac{108 \times w_1}{w_2}$ g. so that the molecular weight of the silver salt is $\frac{w_1}{w_2} \times 108n$

$$\therefore \text{The mol. wt. of the acid} = \frac{w_1}{w_2} \times 108n - 108n + n.$$

(n atoms of silver being replaced by n atoms of hydrogen).

Example : 0.5073 g. of the silver salt of a monobasic acid gave 0.2780 g. of Ag. Calculate its mol. wt.

0.5073 g. of silver salt gave 0.2780 g. of silver.

$$\therefore \text{Mol. wt. of silver salt} = \frac{0.5073}{0.2780} \times 108.$$

Since the acid is monobasic, the mol. wt. of the acid is

$$\frac{0.5073}{0.2780} \times 108 - 108 + 1 = 90.06.$$

Mol. wts. of organic bases.—When the acidity of a base is known, its molecular weight can be calculated from the equivalent weight. The latter is usually determined by analysing the additive compounds that most organic bases form, like ammonia, in hydrochloric acid solution with platinum chloride. These are known as platinichlorides or chloroplatinates, $B_2H_2PtCl_6$ (if B is a monoacidic base) or BH_2PtCl_6 (when B is diacidic). These are crystalline and on ignition, give metallic platinum. The weight of platinum from a definite weight of chloroplatinate is determined.

The base is dissolved in HCl and a solution of platinum chloride, $PtCl_4$, added. The yellow, crystalline chloroplatinate that separates is filtered, washed and dried. A weighed quantity is then ignited in a crucible.

Let w_1 g. of the platinum salt yield w_2 g. of Pt. on ignition, and n be the acidity. Then, 195.2 g. of Pt. (at. wt.) will be obtained from $\frac{w_1}{w_2} \times 195.2$ g. of the salt, which is the molecular weight of the salt.

$$H_2PtCl_6 = 2 + 195.2 + 6 \times 35.5 = 410.2.$$

$$\therefore \text{The mol. wt. of the base} = \frac{w_1}{w_2} \times 195.2 - 410.2, \text{ if it be diacidic.}$$

But if the base be monoacidic, the figure should be halved.

Example : Calculate the molecular weight of a monoacidic base, 0.596 g. of whose chloroplatinate gave on ignition 0.195 g. of platinum.

0.596 g. platinichloride gave 0.195 g. of Pt. whence mol. wt. of

$$\text{salt} = \frac{0.596}{0.195} \times 195 \text{ or } 596.$$

$$\therefore \text{Mol. wt. of base} = \frac{596 - 410.2}{2} = \frac{185.8}{2} = 92.9.$$

The equivalent wt. of a base may also be found by titrating with standard alkali in presence of phenolphthalein a solution of a crystal-

line salt of the base with an acid. The weight of the salt combined with one equivalent of the acid is thus obtained, from which the equivalent wt. of the acid is deducted to get the equivalent wt. of the base.

There are special methods based on the measurement of osmotic pressure, viscosity or rate of sedimentation (by an ultracentrifuge) for determining the mol. wt. of high-molecular compounds like proteins, resins, cellulose, starch, etc.

QUESTIONS

1. A monacid organic base gave on analysis the following results : 0.1413 g. of substance gave 0.3582 g. of CO_2 and 0.1904 g. of H_2O .

0.1237 g. of substance gave 17.85 c.c. of dry nitrogen at 27°C . and 750 mm.

Its platinichloride contains 33.4% Pt. Determine its molecular formula. (B.Sc. Hons., C.U. 1923).

2. Calculate the molecular formula of a monacid organic base containing only H_2 , N_2 and C from the following data.

0.2141 g. gave 0.6160 g. of CO_2 and 0.1621 g. of water. 0.3120 g. of its platinichloride gave on ignition 0.097 g. Pt. (B.Sc. Pass All. Uni. 1934).

3. On analysis an organic compound was found to contain C = 43.98%, Cl = 37.18%, H = 2.09%. Calculate the empirical formula. Given that the compound is a monobasic acid, write the molecular formula. (B.Sc. London, 1925).

4. 0.6 g. of a substance was dissolved in 10 g. of acetone. An elevation of 1.67°C was observed in the b.p. of the solvent. Calculate the mol. wt. of the substance. K for acetone is 16.7. (B.Sc. Punjab, 1914).

5. In a determination of mol. wt. of a substance by Victor Meyer's method, 0.1680 g. of the substance gave 49.4 c.c. of vapour at 20°C and 740 mm. Calculate the mol. wt. of the substance. (B.Sc. Agri., Punjab, 1926).

6. Two solutions containing respectively 7.5 g. of urea, CON_2H_4 , and 42.75 g. of a substance X in 1000 g. of water, freeze at the same temperature. Calculate the mol. wt. of X.

7. Calculate the mol. wt. of an unknown organic liquid from the following data obtained from Victor Meyer's experiment at 14° and 718 mm.

Wt. of substance taken—0.2427 g.

Vol. of air measured—24.3 c.c.

Aqueous tension—12 mm.

8. Describe in some detail how you would find out the mol. wt. of a substance in solution by determining accurately the lowering of the freezing point of the solvent.

In an experiment of this kind, a solution of 1.9 g. of substance in 128 g. of water froze at -0.36°C . Calculate the mol. wt. of the substance ($K = 18.6^\circ\text{C}$ per 100 g. of water). (Cambridge Higher School Certificate).

9. A monobasic organic acid gave on combustion the following percentage composition: Carbon, 39.95 and hydrogen, 6.69. 0.2565 g. of the silver salt of the acid gave on ignition 0.1659 g. of silver. Calculate the molecular formula of the acid. (B.A. & B.Sc. Degree Exam., 1942, Andhra Uni.).

CHAPTER IV

STRUCTURE OF MOLECULES AND CLASSIFICATION OF ORGANIC COMPOUNDS

Atomic structure.—Atoms of which matter is composed, consist of three distinct sub-atomic particles called *electron*, *neutron* and *proton*. The *electron* is negatively charged, carrying 1.602×10^{-9} coulombs or 4.8024×10^{-10} e.s.u. of electricity; it has a mass 9.11×10^{-28} g. which is $\frac{1}{1838}$ of the mass of the hydrogen atom or 0.000544 on the ordinary atomic scale. Cathode rays, produced during electric discharge through a gas at extremely low pressure in a vacuum tube, consist of electrons. Metals at high temperature emit electrons as do radio-active substances during disintegration. Electrons from different kinds of matter are identical. The *neutron*, as the name signifies, is electrically neutral; it has a mass 1.00893 on the atomic weight scale (oxygen = 16.00) which is almost the same as the mass of the proton. Neutrons are discharged when beryllium is bombarded with α -particles; heavy hydrogen (deuterium) under the influence of X-ray of short wave-length, also emits neutron. Neutrons are very effective in disintegrating atomic nucleus (in atom bombs, for example) which does not repel the neutral neutrons. The *proton* has a positive charge which is equal in magnitude to that of the electron, viz. 4.8024×10^{-10} e.s.u. It has a mass 1.0081 (oxygen = 16.00). When an electric discharge is passed through hydrogen at low pressure, protons move towards the cathode. It may be noted that the proton and the hydrogen atom have the same mass. Both the proton and the neutron have diameter of the order of 10^{-13} cm. The neutron may be looked upon as a fusion product of the proton and the electron.

According to the modern theory, the atom of an element consists of

(i) A positively charged *nucleus* containing protons and neutrons, associated together in a manner not yet clearly understood. The number of protons is equal to the atomic number of the element, which indicates its position in the Periodic Table. The sum total mass of the protons and the neutrons almost exactly represents the atomic mass inasmuch as the mass of the electrons present in the atom is negligible compared with that of the proton and the neutron. In other words, the atomic weight of an element is virtually equal to the number of protons plus the number of neutrons in its nucleus. The total charge of the protons obviously represents the net positive charge of the nucleus because the neutrons carry no charge.

(ii) A set of electrons, moving round the nucleus in definite orbits, somewhat like the planets round the sun in the solar system, the number of which is equal to the number of protons present in the nucleus. The total negative charge carried by the

planetary electrons thus exactly neutralises the total positive charge of the protons in the nucleus, with the result that the atom as a whole is electrically neutral. The electrostatic attraction between the positive nucleus and the negative electrons accounts for the stability of the atom.

The difference between the atomic weight (oxygen = 16.00) and the atomic number of an element, therefore, gives, to the nearest whole number, the number of neutrons present in the nucleus.

Physical constants of some particles

Particle	Mass (0 = 16)	Diameter (cm)	Electric charge	
			sign	magnitude
Electron	0.000544	—	negative	4.8024×10^{-10} e.s.u.
Proton	1.0081	$\sim 10^{-13}$	positive	4.8024×10^{-10} e.s.u.
Neutron	1.0089	$\sim 10^{-13}$	neutral	zero
Hydrogen atom	1.0081	0.6×10^{-8}	neutral	zero
Carbon atom	12.000	1.54×10^{-8}	neutral	zero

The electrons group themselves in definite order in the shells round the nucleus; thus the first shell (*K* shell) contains a maximum of two electrons, the second (*L* shell) has not more than eight, the third (*M* shell) accommodates eighteen at the highest, and so on. In the outermost shell, however, the number of electrons does not exceed eight. The number of electrons in the outer shell of the atom of an element mainly determines its valency; in chemical reactions, only the outer electrons are disturbed.

Structure of individual atoms.—Hydrogen, the first element in the Periodic Table, has the simplest atomic structure; a single proton constitutes the nucleus and a single electron occurs in the outer shell. Helium, the next member, with atomic number 2 and atomic weight

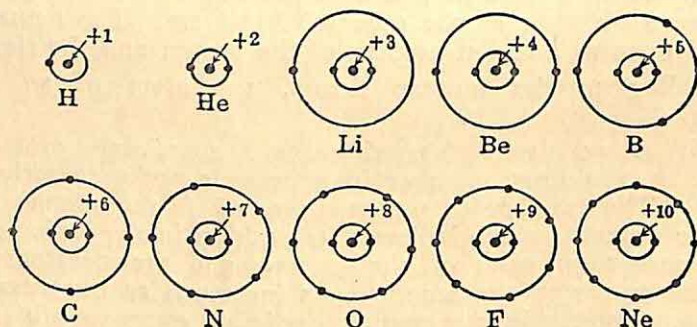


Fig. 18a

4, has a nucleus of 2 protons and 2 neutrons; it has 2 electrons in the outer shell. Lithium, following helium, has atomic number 3 and at. wt. 7; it has 3 protons and 4 neutrons in its nucleus, and 1 electron in *L* and 2 in *K* shell. Carbon has atomic number 6 and at. wt. 12; so it has 6 protons and 6 neutrons in the nucleus, there are 2 electrons in its *K* shell and 4 in the outer ring. Neon, the inert gas following

fluorine, has 10 protons and 10 neutrons in the nucleus and 2 electrons in its K shell and 8 in the L shell. The atomic structures of the first ten elements in the Periodic Table are roughly indicated in Fig. 18a.

Since the noble gases He, Ne, Ar, Kr, Xe and Ra have the maximum number of electrons in the respective outer shells and their complete inertness indicates the exceptional stability of their structure, it is believed that the electronic arrangement of inert gas type *i.e.*, 8 electrons in the outermost shell (2 in the case of He) confers the maximum stability (*octet rule*). We, therefore, assume that in chemical reactions the natural tendency of the atoms taking part is to attain the stable structure of the inert gases either by taking electrons in, or by parting with electrons from, the outermost shell (W. Kossel, 1916). PBr_5 (10 electrons), SF_6 (12 electrons), IF_7 (14 electrons), OsF_8 (16 electrons) are, however, exceptions to the octet rule.

The electronic theory of valency.—Our ideas about the atom and its combining power *i.e.*, valency have undergone radical changes during the last forty years. The nature of the chemical bond is now more clearly understood in the light of modern atomic structure conceived by Rutherford, Bohr, Moseley and others. It is believed that in chemical combination, a change occurs in the number of electrons in the outermost shell of an atom, and that the normal tendency of the atoms, taking part in a chemical reaction, is to adjust the electrons in their external shells so as to attain the electronic configuration of the nearest inert gas in the Periodic Table. There are two distinct ways in which an atom can combine with another *viz.*, (i) by transfer of electron, forming what is called an *ionic, polar, electrovalent* or *electrostatic bond* and (ii) by sharing electrons and forming a *covalent* or *non-polar bond*.

The ionic bond.—Some atoms can attain the inert gas structure by losing or gaining one or more electrons. For example, of the 11 extra-nuclear electrons that sodium has, 2 are in the K shell, 8 in the L shell and only one in the outermost shell, which is its valency electron. Sodium, therefore, readily loses this electron and attains the structure of neon having 10 electrons, 2 in the K shell and 8 in the L shell. By losing one negative charge, sodium becomes a positively charged, mono-

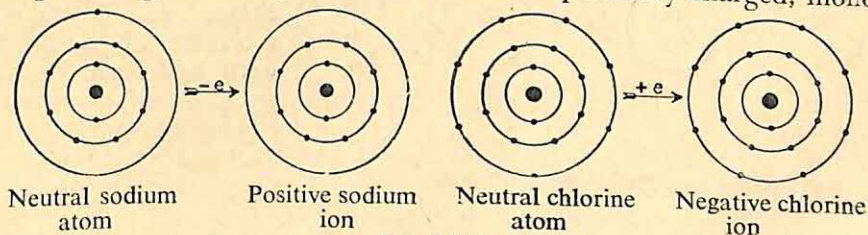
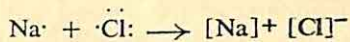


Fig. 18b.

valent ion, Na^+ . Chlorine, on the other hand, has in all 17 electrons of which 2 occur in the K shell, 8 in the L shell and 7 in the outermost shell; these 7 are its valency electrons. Chlorine, therefore, acquires one more electron and attains the electronic structure of argon which has a total of 18 electrons, 2 in the K shell, 8 in the L shell and 8 in the

M shell. Chlorine with an additional negative charge becomes a monovalent negative ion, Cl^- .

When sodium combines with chlorine to give sodium chloride, NaCl , sodium parts with its only electron in the outer shell, which chlorine takes up to complete its octet of outer shell; in solid sodium chloride, the positively charged sodium ion holds the negatively charged chlorine ion in juxtaposition by electrostatic or coulomb forces. It is, therefore, termed *electro-valency* (Langmuir, 1919) or an ionic bond. (Only the outer electrons are indicated by dots below).



There may, of course, be more than one ionic bond between a pair of atoms *e.g.*, in calcium oxide, calcium transfers its two outer electrons to oxygen that has six in its outer ring, Ca^{++} and O^{--} thus result; these are held together in calcium oxide by ionic bonds as in NaCl . An ion may consist of more than one atom, *e.g.*, the ammonium ion, NH_4^+ , or the nitrate ion, NO_3^- . The ionic or polar bond breaks readily when the compound is dissolved in an ionising solvent such as water, giving rise to oppositely charged and independently mobile ions which conduct electricity. Thus there exists no intimate structural connection between the ions in a polar compound, the individual atoms, having ionic bonds between them, are not oriented in any fixed manner. This ionic connection in a polar compound, strictly speaking, is not a linkage. Compounds with ionic bonds have usually low volatility; they melt or boil at high temperature and rarely burn readily. These include most inorganic and some organic compounds. They are generally reactive chemically. They dissolve in water but not in non-polar solvents like benzene or ether. An atom or a group of atoms never exhibits an electrovalency higher than four.

The covalent bond.—As already stated, the atomic structure of the inert gases may be attained by the mutual sharing of electrons

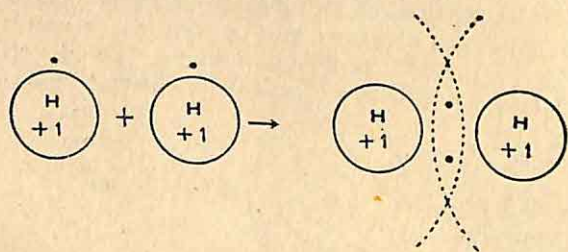


Fig. 18c. Hydrogen molecule.

18c). Hydrogen is normally univalent; it, however, exhibits uni-electrovalence sometimes, *e.g.*, in sodium hydride, NaH .

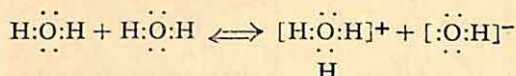


Similarly, in the formation of water, the oxygen atom having 6 electrons in its outer ring, shares one with each of two hydrogen atoms and attains the electronic configuration of neon by completing its octet (Fig. 18d).

But water is not a purely covalent compound inasmuch as it has a small electrical conductivity. Therefore, it slightly ionises as



The oxygen of an undissociated water molecule donates one of its lone pairs of electrons to this proton forming a hydronium or hydroxonium ion, H_3O^+ . The net result is



In the donating water molecule, the oxygen becomes tricovalent uni-electrovalent.

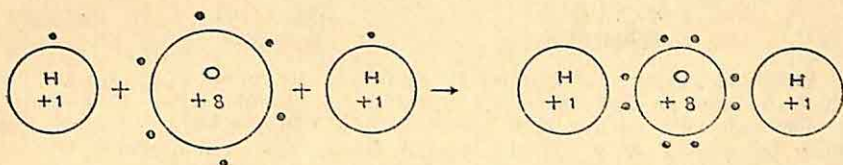


Fig. 18d. Water molecule.

An atom of carbon with 4 electrons in its outermost shell likewise shares one electron with each of 4 hydrogen atoms and forms methane, CH_4 , attaining thereby the structure of neon (Fig. 18e). Carbon is almost invariably quadrivalent.

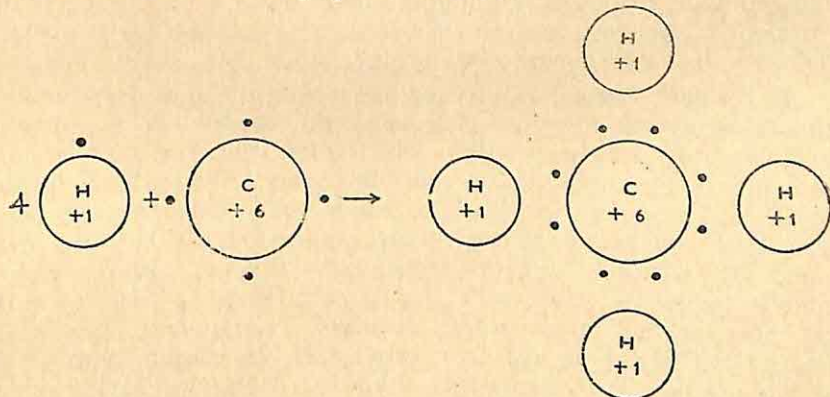
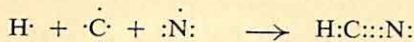


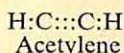
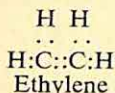
Fig. 18e. Methane molecule.

A bond in these cases is formed between two atoms by a pair of electrons or *duplets* held jointly by both. It is called a *covalent bond* (G. N. Lewis, 1916). All inorganic compounds that are non-electrolytes as well as most organic compounds have covalent linkages. They do not usually dissociate as ions in solution and so are non-conductor of electricity. They generally have low melting and boiling points, burn more or less readily and are soluble in non-ionizing solvents such as hydrocarbons. Oxygen is di-, and nitrogen is tri-covalent. The maximum covalency an atom can exhibit is represented by the difference of the number of electrons it has in the outer ring and the

number the inert gas, following it in the Periodic Table, has in its external shell. Polycovalent atoms may combine by sharing two or more electron pairs; e.g., in carbon dioxide and hydrogen cyanide the linkages are



A similar mode of combination exists between two carbon atoms in ethylene, C_2H_4 , and acetylene, C_2H_2 .



Each shared pair (or duplet) is equivalent to an ordinary valence bond. two such pairs or four electrons constitute a double bond, three pairs or six electrons make a triple bond. A quadruple bond between two atoms would imply the sharing of 4 duplets between them; this is impossible unless the atom be flat. That is why such bonds are not met with.

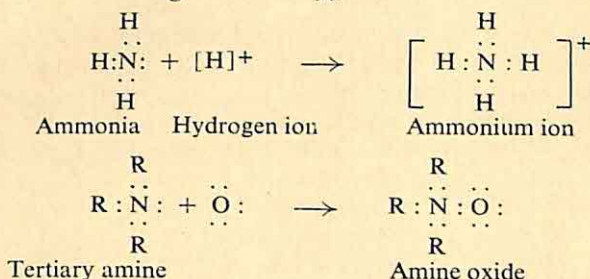
Some compounds may have both covalent and electrovalent bonds, e.g., in ammonium chloride, NH_4Cl , N and 3H are linked by covalent bonds while NH_4^+ and Cl^- are connected by an electrovalent bond. In ammonium salts, therefore, nitrogen is quadricovalent uni-electrovalent. Certain compounds may behave as covalent as well as electrovalent form under different conditions, e.g., hydrogen chloride is covalent in gaseous state but electrovalent in aqueous solution wherein it behaves as a strong electrolyte (vide Chapter IX).

A covalent bond, unlike an electrovalent bond, represents an intimate structural connection between the atoms; in the molecule, the atoms have definite positions which they cannot change normally. Consequently, the molecule has a definite shape. We shall see presently that the valency bonds of carbon, which are covalent, make definite angles with one another. Organic compounds which are mostly formed by covalent linkages, dissolve in organic liquids which are generally non-polar; they do not, as a rule, ionise in solution as their atoms cannot fall apart when dissolved. Compounds like sodium acetate, CH_3COONa , or sodium methyl, CH_3Na , contain both covalent and ionic bonds like ammonium chloride. Molecules having opposite

charges on its atoms such as Na^+Cl^- and $\text{CH}_3\text{N}^+\text{C}(=\text{O})\text{O}^-$ are called *polar*; they are more reactive and less volatile than otherwise similar non-polar compounds.

Co-ordinate covalency.—In the third type of chemical bonding, closely resembling the covalent bond, the electron pair is *not equally shared*, but supplied by one atom only; the other atom receives them. The former is called *donor* and the latter *acceptor*. An apparently saturated compound such as ammonia, NH_3 , combines with HCl to form an ammonium ion, NH_4^+ , as follows. In ammonia, the outer shell of nitrogen is complete with 8 electrons; one pair of

electrons is, however, unshared, *i.e.*, not attached to any other atom. This *lone pair* has a tendency to combine with another atom and complete the octet (duplet in the case of hydrogen) of the latter. Ammonia cannot unite with a hydrogen atom by sharing electron inasmuch as the outer octet of nitrogen would be exceeded thereby. It can, however, combine with a hydrogen ion (which has lost its electron) as shown below; the positive charge of the hydrogen ion is assumed by the ammonium ion. Tertiary amines, as well shall see later on, likewise combine with oxygen to give amine oxides, R_3NO , the nitrogen atom supplying both the electrons for the formation of a bond between nitrogen and oxygen.

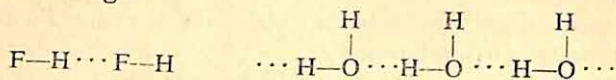


This is known as *co-ordinate* or *dative link* as one atom donates the lone pair of electrons. The structure is indicated by an arrow-head pointing from the donor towards the acceptor atom *e.g.*, $R_3N \rightarrow O$. The virtual transfer of a duplet from the R_3N molecule which is electrically neutral, to the neutral oxygen atom disturbs the electrical neutrality of both; in amine oxide, the R_3N portion has a tendency to assume a positive charge and the oxygen atom a negative charge. This is usually indicated by positive and negative signs (often in circles) placed against the donor and the acceptor atoms respectively, *e.g.*, $R_3N^+O^-$.

A co-ordinate bond, therefore, differs from the covalent bond only in its mode of formation; it has an additional bonding due to polar charges. Some of its characteristics are consequently common to covalent as well as electrovalent bonds. So it is also called a *semi-polar* or *semi-ionic bond*. The line of demarcation between covalent and electrovalent bonds is not quite sharp; many compounds with covalent linkage exhibit polar characters due to unequal sharing of electrons between atoms. When the sharing of electrons between adjacent atoms in a molecule is equal, it is called *homo-polar*; if not, the molecule is *hetero-polar*.

Hydrogen bonding.—There are convincing evidences to show that hydrogen, though univalent, can under certain circumstances, behave as a bivalent element, holding two atoms with sufficient tenacity. The proton of hydrogen apparently forms a bridge between the atom with which the hydrogen atom is already linked in the chemical sense and a second atom in the same or another molecule. This is called *hydrogen bridge* or *hydrogen bond*. Hydrogen usually forms such bonds between electronegative elements with small atomic

radius, e.g., N, O, F and S, the mechanism of which is not yet quite clear. The strength of the bond generally increases with the increasing electronegative character of the atoms bridged by hydrogen. The hydrogen bond is also formed between carbon attached to a strongly electronegative group and oxygen or nitrogen. The bond is usually indicated by a dotted line, but sometimes an arrow is also used. Dimerisation of hydrogen fluoride, high boiling point of water (which has a low molecular weight) due to association, etc. are accounted for by hydrogen bonding:



Similarly, association of alcohols, dimeric nature of formic acid, etc. as also the miscibility of lower alcohols with water may be satisfactorily explained by hydrogen bonding, as we shall see later on. It is an electrostatic bond between positive hydrogen and negative oxygen or fluorine. Electron diffraction methods have shown that the oxygen-to-oxygen distance in each $\text{O}-\text{H} \cdots \text{O}$ bond is 2.67 Å but the $\text{O}-\text{H}$ distance from one oxygen is 1.0 Å and from another 1.67 Å. The hydrogen is closer to the oxygen to which it is linked covalently than to the one to which it is attracted electrostatically. The hydrogen bond is much weaker than a covalent bond, and very much similar to van der Waals forces. *Intramolecular* hydrogen bonding leads to ring (5- or 6-membered) formation or chelation, and *intermolecular* hydrogen bonding results in association. Energy required to break a hydrogen bond is only about 10 kg.cal. mole for $\text{H}-\text{F} \cdots \text{H}$, 7 for $\text{H}-\text{O} \cdots \text{H}$ and 2 for $\text{H}-\text{N} \cdots \text{H}$, compared with the bond energy of $\text{O}-\text{H}$ (110.2), $\text{H}-\text{H}$ (103.4), $\text{C}-\text{H}$ (87.3) and $\text{C}-\text{C}$ (58.6) in covalent bonds in gaseous molecules.

The valency of carbon.—The existence of a vast number of stable organic compounds may be explained by the electronic structure of the carbon atom; it occupies the central position in the first period of the Periodic Table. It is neither electro-positive nor electro-negative. Its affinity for electropositive elements like hydrogen is the same as that for electronegative elements such as oxygen or chlorine. So carbon forms equally strong covalent bonds with H, O, S and the halogens as with itself. With four electrons in the outer shell, it can combine with four univalent atoms or groups of atoms. It thus attains an inert gas structure having an outer ring of eight electrons. This octet is fully shared and cannot expand, 4 being the maximum valency of carbon. Hence carbon atoms in organic compounds can act neither as donors nor as acceptors. The neutral carbon atom would require 4 electrons to form the carbon ion, C^{4-} , this is quite large. Carbon, in most of its compounds, is covalent; no organic compound is known to give simple carbon ions, C^{4-} or C^{4+} ; the atom is too small to gain or lose four electrons. Carbon atoms form covalent bonds with one another almost indefinitely—a unique property which is rarely exhibited by any other element except to a limited extent by silicon and nitrogen. This and the tetra-valency of carbon were recognised by Kekulé as early as 1858, which laid the foundation of structural organic chemistry. His idea of valency was a structural link, indicated

in the classical way by a stroke, between the atoms bonded together. We now recognise his symbol of valency as a covalent bond, each stroke representing a pair of shared electrons. The four covalent bonds of carbon subtend equal angles *viz.*, $109^{\circ}28'$ with one another; with the carbon atom at the centre of a regular tetrahedron, these covalent bonds are directed towards the four corners (Fig. 18f). X-ray analysis of the diamond crystal shows that each carbon atom is linked with four adjacent carbon atoms in the same pattern. It has also been established that all the four valencies of carbon are equivalent. Methane, CH_4 , has the following graphical formula or structure. For convenience, however, it is represented in *one* plane by (i); the spatial arrangement is shown in Fig. 18g.

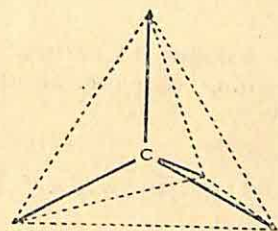


Fig. 18f.
Valency bonds of carbon.

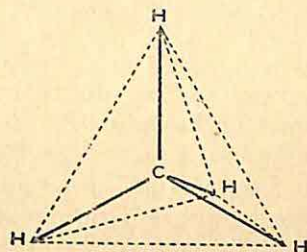
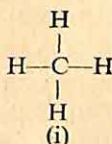
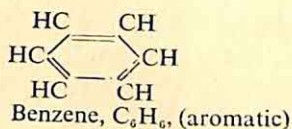
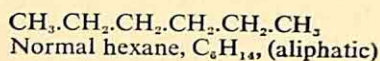


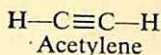
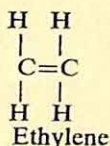
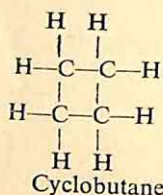
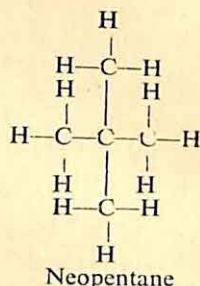
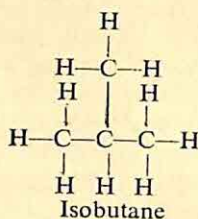
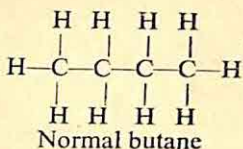
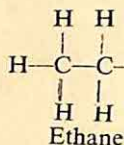
Fig. 18g. Methane molecule.

Classification of organic compounds.—The study of the vast number of carbon compounds has been simplified by dividing them into a small number of groups or families such as hydrocarbons, alcohols, fatty acids, aldehydes, ketones, etc. Members of each family possess certain characteristic properties by which they can be distinguished; they are prepared by more or less similar methods. Individual members of each group, however, differ from one another in some physical properties in a graded manner, *e.g.*, the melting point gradually rises as the molecular weight increases. The contrast between one family and another as regards physical and chemical properties as well as mode of preparation, is, however, marked. In our study, therefore, we pay more attention to family characteristics than to individual members. For convenience, organic compounds have been divided, according to similarity in structure, into two broad classes, *viz.*, (i) *aliphatic* and (ii) *aromatic*.

The aliphatic are generally open-chain compounds; the term comes from Greek *aleiphar*, meaning fat, since vegetable and animal fats have open-chain structure. The aromatic are closed-chain or ring compounds, so called originally because of the *aroma* or smell which many of them possess. But some closed-chain compounds belong to the aliphatic group and numerous compounds devoid of aroma are aromatic.



Linking of carbon atoms.—Carbon atoms, as already stated, can combine with one another by one or more covalent bonds. Thus we have



When several carbon atoms unite, a *carbon chain*—straight (as in normal butane) or branched (as in isobutane or neopentane)—may be formed; it may also be closed as in the case of cyclobutane.

If in a molecule the carbon atoms are linked with one another by single covalent bonds, it is *saturated*; such compounds form derivatives only by the replacement of an atom or group by another. Methane, ethane, etc. are saturated compounds. If there be one or more pairs of carbon atoms in the molecule, connected by two or three covalent bonds, the compound is *unsaturated*. These add on monovalent atoms or groups to form derivatives, *e.g.*, ethylene and acetylene.

Compounds containing unsaturated groups such as $\text{C}=\text{O}$, $\text{C}\equiv\text{N}$, $\text{N}=\text{O}$, etc. are also unsaturated in the accepted sense of the term, inasmuch as they undergo addition reactions. Unsaturation may as well be confined to a single atom in the molecule, *e.g.*, triphenylmethyl, $(\text{C}_6\text{H}_5)_3\text{C}$. We shall, however, in this elementary book restrict the term unsaturated to compounds having multiple bonds between carbon atoms only.

CHAPTER V

The Aliphatic saturated hydrocarbons: the paraffins, C_nH_{2n+2}

The simplest organic compounds are the hydrocarbons, compounds of carbon and hydrogen. Others may be considered as derived from them by direct or indirect replacement of hydrogen by other atoms or groups. The aliphatic or open-chain hydrocarbons may be saturated or unsaturated (p. 40). The former, briefly called *alkanes*, are more commonly known as '*paraffins*'; the first member of the paraffin family is methane.

Methane, CH_4 , is a gas often found issuing out from marshy lands, whence the name marsh-gas. It is formed by bacterial decomposition of vegetable matter under water. A little phosphine, PH_3 , accompanies the gas, which makes it spontaneously inflammable, causing the formation of 'will-o'-the-wisp'. Methane is the chief constituent (about 85%) of natural gas from oil-wells in petroleum districts in U.S.A. The 'eternal fires of Baku' were due to the ignition of natural gas from the oil-fields. The gas is also found in coal-mines (known as 'fire-damp'; German *dampf* vapour) and was in the past the cause of severe explosions in mines. Coal-gas contains 35-40% methane by volume. It is present in human intestinal gases—may be up to 50% after a pulse diet. During disposal of sewage by the activated sludge method, a gas containing about 70% of methane is evolved.

Preparation : (1) Methane is usually made in the laboratory by heating fused sodium acetate with three times its weight of soda-lime (quick-lime slaked with conc. caustic soda solution and thoroughly dried) in a hard glass test-tube, or better, in a copper flask. The gas is collected over water. It is not pure, containing ethylene, hydrogen, etc.; it has a bad odour.

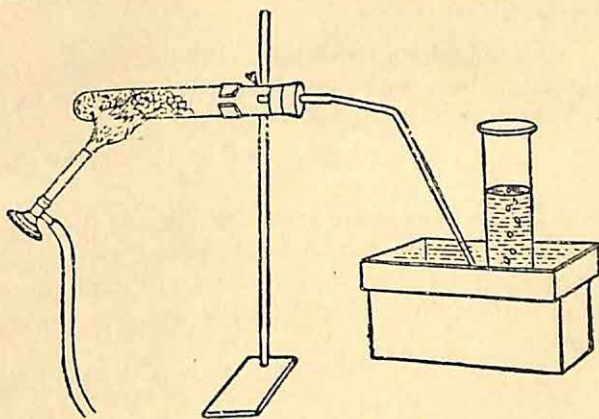
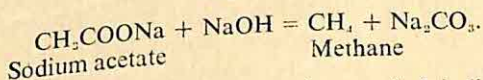
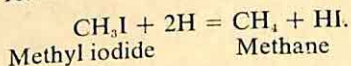


Fig. 19. Preparation of methane.



(2) The pure gas is obtained by reacting methyl iodide with zinc-copper couple in presence of alcohol or water. Nascent hydrogen, liberated from the latter by the couple, reacts with methyl iodide :



About 25 g. of pure, granulated zinc are added to a solution of copper sulphate.

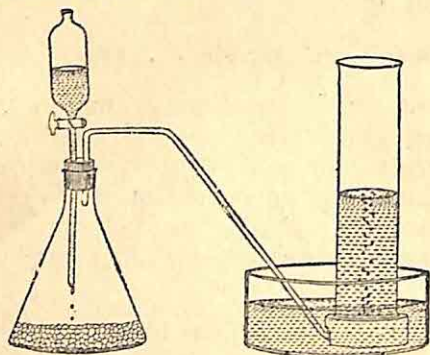
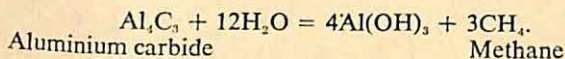


Fig. 20. Preparation of methane from methyl iodide.

zinc is thus coated with a thin layer of copper. The granules are taken out and washed thoroughly with water which is then removed with alcohol. Zinc-copper couple thus prepared is taken in a conical flask fitted with a separating funnel and a delivery tube (Fig. 20). Some alcohol and 2-3 drops of dilute H_2SO_4 are added to the flask. A solution of methyl iodide in 95% alcohol (1:1) is gradually added from the separating funnel. A brisk evolution of methane takes place in the cold. The gas is collected over water. Any methyl iodide accompanying methane may be removed by inserting an empty U-tube, surrounded with freezing

mixture, at the middle of the delivery tube. Aluminium-mercury couple (made by dipping aluminium foil into mercuric chloride solution) may replace zinc-copper couple.

(3) Water decomposes aluminium carbide at ordinary temperature to methane.



The carbide in small lumps is taken in a flask fitted with a delivery tube. Water is added slowly through a tap-funnel, the gas is collected over water. The insoluble aluminium hydroxide, $\text{Al}(\text{OH})_3$, deposits on the lumps of carbide and the reaction slackens after sometime. This may be avoided if water be replaced by dilute HCl .

(4) **Sabatier's method.**—When carbon monoxide (or dioxide) is passed over finely divided, reduced nickel at 250° (or 300°) together with hydrogen, methane is formed.

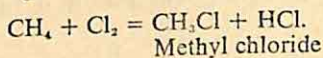


(5) Methane may also be formed by direct combination of its elements. When hydrogen is passed over carbon at about 1200° in a porcelain tube, or an electric arc is maintained between carbon poles in an atmosphere of pure hydrogen, we get methane. But the yield is poor.

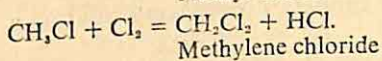


Properties.—Methane is a colourless, non-poisonous gas with no taste or smell. Cooled by liquid air, methane becomes a colourless liquid (b.p. -164°) and finally, a colourless solid at -186° . The gas, much lighter than air, is slightly soluble in alcohol. Methane is extremely stable; even at 1200° it undergoes only slight decomposition producing ethane, traces of benzene, etc. The gas burns in air with a non-luminous flame, and forms a highly explosive mixture with air. With excess of oxygen, the products of combustion are CO_2 and H_2O .

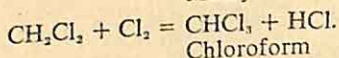
Methane is resistant to acids, alkalis, metals, ordinary hydrolysing, oxidising and reducing agents. This is on the whole true of other saturated hydrocarbons which are consequently known as paraffins (*parum* little, *affinis* affinity). Halogens, however, react with methane. Fluorine does so violently, producing carbon and hydrofluoric acid. Chlorine cannot attack methane in the dark, but in direct sunlight, a mixture of methane and chlorine explodes: $2\text{Cl}_2 + \text{CH}_4 = \text{C} + 4\text{HCl}$. In diffused light, hydrogen is slowly replaced one by one:



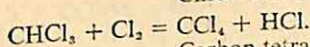
Methyl chloride



Methylene chloride



Chloroform



Carbon tetrachloride

The process is called *substitution* and the resultant compound substitution product. Bromine gives similar derivatives, but iodine yields none. The above reactions are theoretically important, but seldom utilised due to their slowness, the difficulty of isolating the products and also the cost involved.

The mechanism of the reaction is as follows. Light, heat or other catalysts split a chlorine molecule into two chlorine atoms. A chlorine atom removes a hydrogen atom from methane, a free methyl radical, $\cdot\text{CH}_3$, and HCl thus result. $\cdot\text{CH}_3$ then reacts with a chlorine molecule to form methyl chloride and a chlorine atom. This chain reaction goes on until carbon tetrachloride is formed.

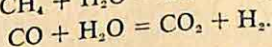
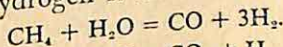


Ozonised oxygen converts methane into formaldehyde; it thus serves as a delicate test for methane as formaldehyde can be readily detected by colour test.



Methane Formaldehyde

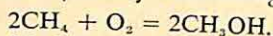
A mixture of methane and steam, passed at 800° over nickel catalyst, yields hydrogen and carbon monoxide. The latter reacts with steam at 500° in presence of ferric oxide to give carbon dioxide and hydrogen. Industrial hydrogen is thus made.



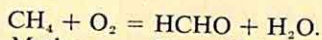
Methane gives on combustion nearly 1000 B.T.U. of heat per cu. ft. Natural gas is used chiefly as fuel in U.S.A. In Roumania, it is abundant enough to be burnt in air for obtaining nitrogen which is combined with CaC_2 to produce calcium cyanamide, CaCN_2 , a manure.

Methyl alcohol and formaldehyde are made by the *partial* oxidation of methane under suitable conditions. Methane is obtained by

the bacterial decomposition (e.g., with horse dung) of waste vegetable matter (chiefly consisting of cellulose) below 60°.



Methane Methyl alcohol



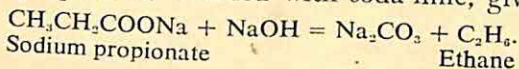
Methane Formaldehyde

U.S.A. makes carbon black (about a billion lb. yearly) by the incomplete combustion of natural gas. The carbon is used in automobile tyres, printer's ink, gramophone records, typewriter ribbons, paints, etc.

Ethane, C_2H_6 , like methane, occurs in natural gas (about 10%) and coal-gas.

Preparation.—Methods of preparing methane generally apply to ethane.

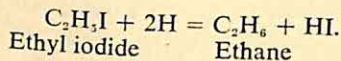
- (1) Sodium propionate, distilled with soda-lime, gives ethane:



Sodium propionate

Ethane

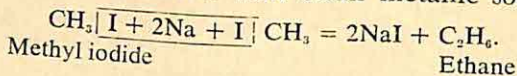
- (2) Zinc-copper couple in presence of ethyl alcohol reduces ethyl iodide to pure ethane:



Ethyl iodide

Ethane

- (3) Ethane is also formed when methyl iodide or bromide reacts in dry ethereal solution with clean metallic sodium.

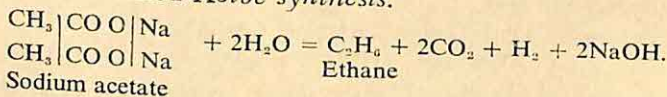


Methyl iodide

Ethane

This is **Wurtz Reaction**. Frankland first effected the synthesis with zinc. C. A. Wurtz (1817-1884), a French chemist and pupil of Liebig, discovered the reaction in 1855. With two different alkyl halides, three hydrocarbons are formed; their separation is not, however, easy.

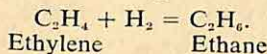
- (4) Electrolysis of a concentrated, aqueous solution of an alkali acetate gives ethane and carbon dioxide at the anode. This was discovered by the German chemist A. W. H. Kolbe in 1848 and is called *Kolbe synthesis*.



Sodium acetate

Ethane

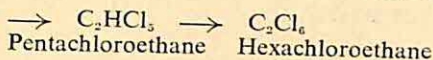
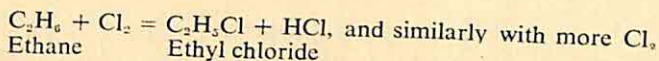
- (5) A mixture of ethylene and hydrogen, passed over finely divided nickel at high temperature, gives ethane:



Ethylene

Ethane

Properties.—Ethane closely resembles methane in physical and chemical properties, e.g., it is a colourless, odourless and tasteless gas, practically insoluble in water but soluble in alcohol. The gas can be liquefied at 4° under 46 atmospheres pressure; the colourless liquid boils at -89°. It is quite as stable as methane and equally inert chemically. With chlorine, similar substitution products are obtained and finally C_2Cl_6 .



Propane, C_3H_8 , and **butane**, C_4H_{10} , follow ethane in the paraffin series. **Propane** occurs appreciably in 'casing-head gas' (natural gas coming from oil-wells up the casing pipe during drilling). It is obtained therefrom by absorbing with active charcoal and expelling from the latter by steam. It may be prepared by any of the general methods (p. 49). It resembles methane and ethane, and gives similar substitution products with chlorine; it is, however, slightly more reactive. Liquid propane is employed in refining lubricating oils. There are two **butanes**, normal and iso-, both occur in natural gas (also in casinghead gas) and are obtained therefrom. Normal butane may be prepared by Wurtz method from ethyl iodide, $\text{C}_2\text{H}_5\text{I}$, and sodium, and iso-butane by reducing iso-butyl iodide, $(\text{CH}_3)_2\text{CH}.\text{CH}_2\text{I}$. They resemble propane. In presence of AlCl_3 and HCl , *n*-butane passes on reversibly to *iso*-butane. Mixed with dry air, butane is employed as a standard fuel for the heat treatment of specific steels. Butanes are also mixed with water-gas to make the flame luminous. In U.S.A. liquefied propane and butanes serve as cooking fuel.

Pentanes, C_5H_{12} , normal, iso- and neo-, occur in petroleum and natural gas; petroleum ether is mainly a mixture of pentanes and hexanes. Normal pentane, $\text{CH}_3(\text{CH}_2)_3\text{CH}_3$, boils at 36° , isopentane, $(\text{CH}_3)_2\text{CH}.\text{CH}_2.\text{CH}_3$, at 28° and neopentane, $(\text{CH}_3)_4\text{C}$, at 9.4° . The mixture of pentanes is chlorinated mainly to mono-chloro-pentanes and used as solvent. A mixture of alcohols obtained by hydrolysing the chloropentanes is also a commercial solvent. Normal pentane is used in thermometers for measuring low temperature.

There are many other saturated hydrocarbons—about 2000—with increasing number of carbon atoms, such as hexanes, C_6H_{14} , heptanes, C_7H_{16} , octanes, C_8H_{18} , and so on.

Homologous series.—We have seen that methane, ethane, propane, butanes, etc., closely resemble one another; e.g., all are practically insoluble in water, quite stable, chemically inert, give substitution products with chlorine, etc. If the aliphatic hydrocarbons are arranged in order of their increasing molecular weights, they are found to correspond to a general formula, $\text{C}_n\text{H}_{2n+2}$, i.e., if there are *n* carbon atoms in a molecule, it has $2n+2$ hydrogen atoms. Each member differs from its preceding or succeeding one by a $-\text{CH}_2-$ group. A group of closely related compounds that can be expressed by a general molecular formula and in which consecutive members differ by a $-\text{CH}_2-$ group, is called a *Homologous series*; the individual members are termed homologues (Greek *homos* same, *logos* ratio). They can be prepared by similar methods. The chemical properties of members are

more or less similar; their physical properties show a fairly regular gradation with rise in molecular weight (*vide* Table below). There are many homologous series in organic chemistry and each may contain several hundred homologues. The study of organic chemistry is largely a study of the various homologous series.

The paraffins, C_nH_{2n+2}

Name	Formula	m.p. °C	b.p. °C	sp. gr. at 20°/4°	Physical state
Methane	CH_4	-186	-166	·554 0°C	Gas
Ethane	C_2H_6	-172	-89	·546 -84°C	"
Propane	C_3H_8	-189·9	-44·5	·585 -44°C	"
<i>n</i> -Butane	C_4H_{10}	-135	0·6	·601 0°C	"
<i>n</i> -Pentane	C_5H_{12}	-130·5	36	·630 18°C	Liquid
<i>n</i> -Hexane	C_6H_{14}	-94·3	69	·660	"
<i>n</i> -Heptane	C_7H_{16}	-90·0	98·4	·684	"
<i>n</i> -Octane	C_8H_{18}	-56·5	126	·706 15°C	"
<i>n</i> -Nonane	C_9H_{20}	-51	150	·718	"
<i>n</i> -Decane	$C_{10}H_{22}$	-32	174	·730	"
<i>n</i> -Undecane	$C_{11}H_{24}$	-26·5	194·5	·741	"
<i>n</i> -Dodecane	$C_{12}H_{26}$	-12	215	·751	"
<i>n</i> -Tridecane	$C_{13}H_{28}$	-6·2	234	·757	"
<i>n</i> -Tetradecane	$C_{14}H_{30}$	5·5	252·5	·765	"
<i>n</i> -Pentadecane	$C_{15}H_{32}$	10·0	270	·772	"
<i>n</i> -Hexadecane	$C_{16}H_{34}$	18	287·5	·775	Solid
<i>n</i> -Heptacosane	$C_{27}H_{56}$	105	—	—	"

The longest paraffin molecule synthesised so far is *n*-hectane, $C_{106}H_{212}$, m.p. 115°.

Isomerism & molecular structure of the paraffins.—The first three members of the paraffin family *viz.*, methane, ethane and propane, are quite simple and there is only one variety of each. But when we come to the four-carbon-atom paraffin butane, C_4H_{10} , we have *two* different compounds with the *same* molecular formula. Likewise pentane, C_5H_{12} , represents *three*. Their properties are somewhat different. Obviously, the nature and the number of atoms in a molecule cannot alone give a complete picture. Compounds which possess the *same* molecular formula but have different properties (they may not belong to the same homologous series), are called **isomers** (*isos*, equal; *meros*, a part) or isomerides; the phenomenon is known as *isomerism*. Thus C_5H_{12} represents:

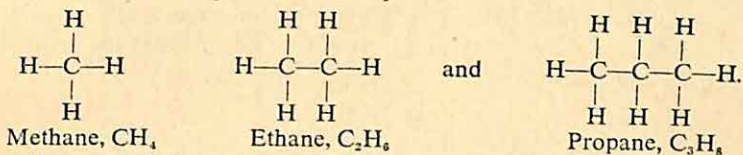
- | | |
|--------------------|---|
| (i) Normal pentane | } Belong to the same homologous series. |
| (ii) Iso-pentane | |
| (iii) Neo-pentane | |

$C_4H_{10}O$ stands for (i) Butyl alcohol	} Belong to different homologous series.
(ii) Di-ethyl ether	

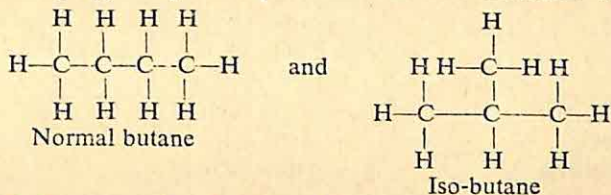
Good many compounds may have the same formula. Thus, $C_8H_{12}O_4$ stands for 66 different compounds and $C_{10}H_{13}O_3N$ for 135, all being known. With increasing molecular weight, the number of possible isomers in a homologous series rapidly increases, their number can be mathematically calculated. Thus there are 5 isomers

for C_6H_{14} , 18 for C_8H_{18} , 35 for C_9H_{20} , 802 for $C_{13}H_{28}$, while $C_{20}H_{42}$ may have 366,319 possible isomers! This brings us to the problem of arrangement of atoms inside a molecule. Two or more compounds having the same atoms in the same number have *different* arrangements of the atoms in the molecules, i.e., *different* structures.

We have to remember that carbon is tetravalent, and all linkages in paraffins are single. The only possible structures for the first three members of the paraffin family are:

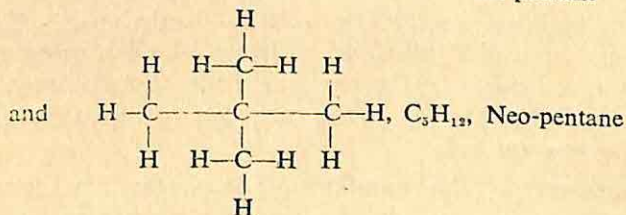
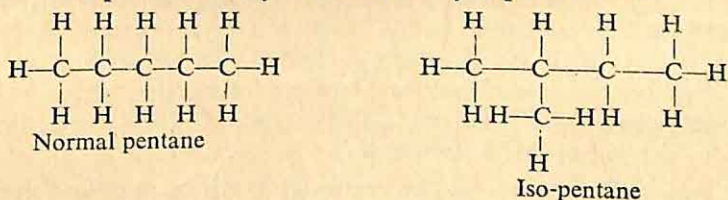


But butane, C_4H_{10} , may be represented in two different ways:



In normal butane, the four carbon atoms are arranged in a straight chain and no carbon is linked to more than two carbon atoms, while in isobutane the chain is branched; it has a carbon attached to three other carbon atoms. This graphical representation of a molecule is its *structural formula* (or *constitution*). The properties and behaviour of a molecule can largely be explained by its constitution.

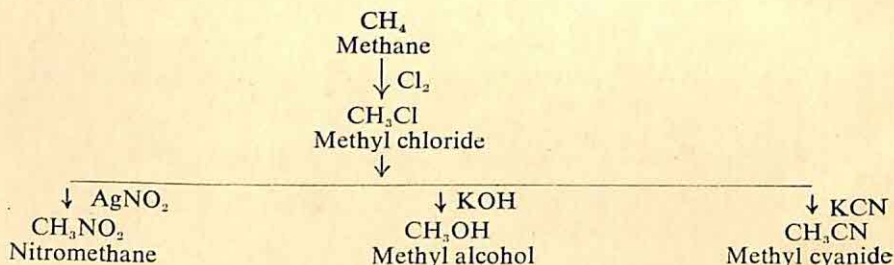
The three pentanes may be structurally represented as



Straight-chain isomers are called *normal* isomers. Normal pentane has $-CH_2-$ groups, known as primary groups. Isopentane has a $-C-H$ group, termed secondary group, while neopentane contains

a carbon atom linked to four other carbon atoms; $\begin{array}{c} | \\ -\text{C}- \\ | \end{array}$ is a tertiary group. Though with the most powerful instrument such arrangements are not directly visible, there are convincing proofs for their existence.

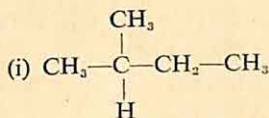
Radicals.—By replacing a hydrogen of methane, CH_4 , by chlorine, we get chloromethane, CH_3Cl , better known as methyl chloride. Other elements, or groups of elements, such as Br, I, or $-\text{NO}_2$, $-\text{OH}$, $-\text{CN}$, etc., can directly or indirectly replace the hydrogen of methane:



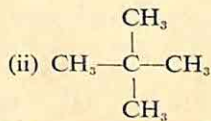
Thus we get a set of compounds— CH_3Cl , CH_3NO_2 , CH_3OH , CH_3CN , etc. in which the $-\text{CH}_3$ group of methane survives chemical reaction; it behaves like inorganic radicals such as $-\text{OH}$, $-\text{NO}_2$, $-\text{NH}_4$, etc. The CH_3- is a monovalent organic radical, termed methyl. Thus, CH_3Br is methyl bromide, CH_3OH is methyl alcohol and so on. Similarly, from ethane, C_2H_6 , we have ethyl chloride, $\text{C}_2\text{H}_5\text{Cl}$, ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$, etc., C_2H_5- being the ethyl radical. C_3H_7- and C_4H_9- are propyl and butyl radicals respectively. The general term for these is **alkyl radical**. A radical is named from the hydrocarbon by replacing the last syllable with -yl. In methyl alcohol the hydroxyl group, $-\text{OH}$, reacts readily and mainly determines its properties; it is called the **functional group**. Similarly, $-\text{CHO}$ and $-\text{CO}-$ are functional groups in aldehydes and ketones.

If two hydrogen atoms be removed from a paraffin, corresponding divalent radicals methylene, $-\text{CH}_2-$, ethylene, $-\text{C}_2\text{H}_4-$, etc., result. These are called **alkylene radicals**. Unlike inorganic radicals, some organic radicals exist in the free state though for a very short while. The mechanism of many organic reactions is satisfactorily explained by free radicals.

Nomenclature of the paraffins.—Except the first four members, methane, ethane, propane and butane, the names of other paraffins are derived from Latin or Greek numerals corresponding to the number of carbon atoms they contain. The names end in ‘-ane’ as names of metals in ‘-um’. There are also other systems of nomenclature. In one, the hydrocarbons are regarded as derivatives of methane, the most highly branched carbon being called the methane carbon. For example,

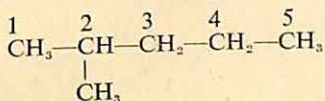


Isopentane or ethyl dimethyl methane

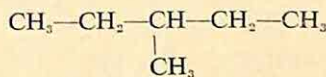


Neopentane or tetramethyl methane

For big molecules, the Geneva system (adopted in 1892 by an international congress of chemists in Geneva), is used. Here the *longest continuous* chain is named according to the number of carbon atoms which are consecutively numbered. The compound is designated as a derivative of this hydrocarbon. For example,

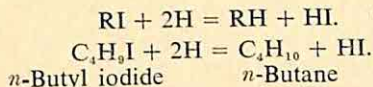


2-Methyl pentane



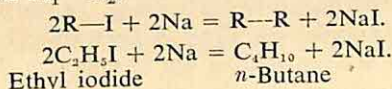
3-Methyl pentane

General methods for preparing paraffins.—(1) By reducing alkyl halides with Zn-Cu couple, Hg-Al couple, or with zinc and dilute HCl, *e.g.*,

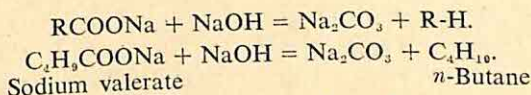


R stands for an alkyl radical such as $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{C}_3\text{H}_7$, $-\text{C}_4\text{H}_9$, etc.

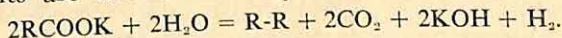
(2) By the action of metallic sodium on alkyl halides (Wurtz). The yield is best with primary halides and if the two alkyl radicals are identical. Tertiary halides give mostly olefines (p. 56). If two different alkyl halides be taken, *three* paraffins are obtained, *viz.*, R_1-R_1 , R_2-R_2 and R_1-R_2 .



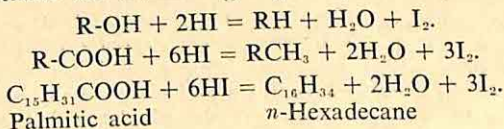
(3) By heating the sodium salt of a fatty acid with soda-lime. The hydrocarbon has one carbon atom less than the parent acid.



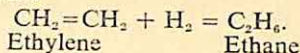
(4) By the electrolysis of a moderately concentrated aqueous solution of potassium or sodium salt of a fatty acid (Kolbe Synthesis): The hydrocarbon has more carbon atoms than the fatty acid. If two fatty acid salts are taken, three hydrocarbons result.



(5) By the reduction of alcohols and fatty acids with HI and red phosphorus (suitable for obtaining higher paraffins):

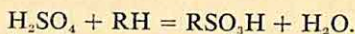


(6) By adding hydrogen in presence of finely divided nickel to unsaturated hydrocarbons:



General properties of the paraffins.—At ordinary temperature methane, ethane, propane and butane are gases; members following them up to hexadecane, $\text{C}_{16}\text{H}_{34}$, are liquid and the higher ones are solid. Paraffins are odourless and tasteless. The gaseous and liquid members are colourless, but the solid paraffins are white. Their boiling points rise fairly regularly with rise in molecular weight but their melting points show an alternation effect, rising and falling with even and odd number of C atoms in the molecule. The difference in physical properties due to an additional $-\text{CH}_2-$ group decreases with increase in molecular size. The more branched the molecule, the lower the b.p. of the isomer (*vide* table on p. 46). Likewise their sp. gr. also increases but the maximum value is 0.78. They are very slightly soluble in water, but fairly soluble in alcohol, benzene, etc. They burn in air giving CO_2 and H_2O .

The paraffins are generally indifferent to oxidising agents. But at high temperature, the higher members (*e.g.*, those from petroleum) give fatty acids on catalytic oxidation. Acids or alkalis ordinarily have no action on them. Fuming H_2SO_4 , however, attacks the branched-chain or higher normal alkanes, *e.g.*, *n*-hexane, giving sulphonic acids, RSO_3H , on heating.



Nitric acid attacks the neo-paraffins which are thus converted into nitroparaffins: $\text{RH} + \text{HNO}_3 = \text{RNO}_2 + \text{H}_2\text{O}$. By direct nitration of the paraffins in the vapour phase at about 450° , nitroparaffins are made commercially in U.S.A. Chlorine and bromine react with paraffins slowly in diffused light yielding substituted halogen derivatives. The process may continue until all the hydrogen has been replaced. Branched paraffins are more reactive than the corresponding straight-chain compounds. Thus 'paraffins' are reactive under suitable conditions. Long-chain hydrocarbons are less stable than short-chain ones.

Petroleum.—Many of the paraffins are present in natural petroleum (*petra*, rock; *oleum*, oil) obtained from underneath the earth (hence often called mineral oil, rock-oil or earth-oil). Their boiling points are so close and so many of them occur together that they can hardly be isolated in pure state. Our knowledge of petroleum is limited; many of the oils have not yet been completely investigated. About thirty hydrocarbons have been isolated from, and identified in, an American oil; these represent only 10% of the oil. Smaller amounts of naphthenes and aromatic compounds are also found in petroleum.

In 1849 George Bissel of U.S.A. read a newspaper report of drilling for salt; the idea of drilling for oil struck him at once. He engaged Colonel Drake for the job, who patiently forced his crude drill near an oil spring at Pennsylvania and got oil at 69 ft. Huge deposits of petroleum occur in the United States, Persia, Russia, Iraq, Mexico, and Indonesia. In comparatively small amounts, it is found in Burma, India, Japan, Rumania and other places. A huge deposit of petroleum has recently been discovered in Arabia—

it is believed to be as large as, if not larger than, the oil deposits of U.S.A. From the commercial point of view, the oil fields of North America are the most important. In 1955, 2.4 billion barrels (1 barrel=42 gallons) of petroleum were produced in U.S.A. alone, this was 43% of the world production which was 5.6 billion barrels. U.S.A. has less than 16% of the known world reserves. In India petroleum is obtained principally from Digboi in Assam, the Khaur and Dhulin fields are in the W. Punjab. The total Indian production in 1941, was 2,270,000 barrels of which nearly 75% came from Assam. In the same year, 496,163 gallons of motor spirit were recovered from natural gas in the Punjab. India requires about 40 crores gallons of petrol per year. Her total kerosene consumption per year is nearly 25 crores gallons, of which 6 crores used to be imported from Burma.

Petroleum, usually associated with natural gas, occurs in porous sand stones below the surface strata and impervious rocks and is pumped up through bore-holes sunk beneath the earth, sometimes to a depth of 5,000-15,000 ft. The pumped oil is then led through underground pipes—some of which are 1,700 miles long—to the refinery at a port or sea-coast for facility of transport.

Treatment of the oil.—Crude petroleum is obtained as a dark-coloured, fluorescent emulsion with sandy soil and water. This is warmed with steam coils in iron vessels with conical base, whereby the emulsion breaks up into two layers. The gases which evolve are led out by a pipe and mainly used as fuel after removing propane and butanes by liquefaction. The upper layer of petroleum is removed and distilled in a tall metal tower called fractionating column into fractions of different boiling points to suit commercial purposes. Temperature limits and names of fractions collected differ in different places. The table on p. 53 gives the average fractions of U.S.A. petroleum. The black residue left in the retorts is petroleum pitch or asphalt, used as a road surfacing and roofing material, protective paint, and in the manufacture of rubber.

The fractions are further purified by re-fractionation. The light, low-boiling fractions are in great demand for automobiles. They are also used in dry cleaning and extracting oils. Kerosene, following it, is purified by treating with concentrated sulphuric acid or liquid sulphur dioxide, which removes unsaturated compounds and reduces the aromatic content, and then with caustic soda, and redistillation. It is used as a turbo-jet fuel in jet aircraft, gas turbines, oil stoves and as illuminant. The residue remaining after the removal of kerosene is further separated above 300° with superheated steam to give the valuable *lubricating oil* and *paraffin wax*. The latter is separated from lubricating oil by chilling to about -3° and filtering in a filter-press or by extraction with phenol. The solid thus obtained is 'sweated' by warming in shallow pans with false bottoms to remove the adhering oil. The product, decolorised with charcoal or powdered clay, is used for candle-making, in match industry, for waxed paper, in laundries, etc.

The residual oil, after purification, forms the *liquid paraffin* of pharmacy, a mild laxative. *White oils* are highly refined grades of lubricating oil, used in making ointments, cosmetics, hair oil, etc. *White spirit*, the lighter fraction of kerosene, is used for dry cleaning, in shoe and furniture polishes and as a substitute for turpentine, a paint vehicle.

Deodorised kerosene, made by treating with strong H_2SO_4 , washing and filtering through fuller's earth, is a solvent for liniments, hair-tonics and antiseptics. Grease is a semi-solid lubricant composed of emulsified hydrocarbon oil (lubricating oil) and soda or lime soap with a little water as stabilizer.

Petroleum generally contains sulphur as H_2S and alkyl hydro-sulphide which give it a foul odour; these are separated (for they are oxidised to acids which corrode the engine) by various means, e.g., by absorbents like alumina, by sodium plumbite, etc. Unsaturated hydrocarbons and aromatic compounds (which deposit carbon on the engine during combustion) are removed by strong sulphuric acid. The oil is decolorised with bauxite or liquid sulphur dioxide.

The composition of petroleum varies from place to place and the last residue, pitch, is also different; for example, Burma oils yield no asphalt (*asphaltos*, unchangeable) but solid paraffins only whereas other varieties yield mainly asphalt and very little solid paraffin. The Baku oil contains about 80% of naphthenes but others contain very little of these. Some American petroleum is rich in paraffins, others contain more of alicyclic or aromatic hydrocarbons.

By inflammability of a substance is meant its ability to burn in air. The **flash-point** of an oil is a measure of its inflammability. It is the temperature at which sufficient vapour is produced to explode with air if brought in contact with a flame. It differs from **ignition-point** which is the lowest temperature at which the oil continues to burn after a flame has been applied to its surface. The flash-point of gasoline is -45° , that of motor lubricating oil is 232° . It largely depends on the form of apparatus employed and the manner of determination. The flash-point gives an indication of the volatility of an oil; the higher the value, the more suitable it is as a lubricant. To minimise fire hazard, the flash-point of illuminating oils e.g., kerosene, is generally fixed by law.

Theories of formation of petroleum.—Various theories have been put forward on the origin of petroleum. According to Mendeleeff, metallic carbides e.g., iron carbide, in the lower portion of the earth's crust reacted with steam under considerable heat and pressure and gave petroleum. Moissan actually obtained a petroleum-like liquid by the action of water on uranium carbide. But the theory fails to explain the optical activity of petroleum and also the huge oil deposits. Engler suggested that marine animals were decomposed under high pressure and temperature and gave rise to petroleum. By heating fish-oil and certain animal fats under pressure, a liquid closely resembling American petrol. has been obtained in good yield. The presence of nitrogen and sulphur compounds, optical activity of petroleum and its association with brine strongly support this view. A third theory has it that petroleum was formed from the decomposition of plants under heat and pressure. The presence of nitrogen, sulphur and chlorophyll derivatives can thus be accounted for.

Cracking.—A large demand for petrol or low-boiling fraction for automobiles has led to a method of converting the heavy, high-boiling fraction, immediately following kerosene, into low-boiling quality by 'cracking'. The hydrocarbon vapour is led through tubes or chambers at about 500° under 10-50 p.s.i. pressure. On the hot surface and in presence of catalysts like anhydrous aluminium chloride or specially prepared silica on alumina, the big molecules break down into small ones having much lower boiling points, which serve the purpose of petrol. Carbon may be deposited. By choice of catalysts and temperature, liquids of desired boiling points may be obtained. Cracking

Refinery yields & trade demands (%) of petroleum products (1949-50)

Boiling range	Approx. composition of paraffins	Name of fraction	Average yield (U.S.A.)	World demand
40-200°	C ₅ -C ₁₁	Petrol or gasoline	43.5	26.7
200-300°	C ₁₂ -C ₁₆	Kerosene	5.2	6.6
above 300°	C ₁₃ -C ₁₈	Gas, fuel, or diesel oil	17.5	18.5
Distilled under reduced pressure	C ₁₆ -C ₂₂	Lubricating oils Residual fuel oil	24.2	41.8
„ „	C ₂₀ -C ₃₀	Paraffin wax	0.2	0.1
Residue	C ₃₀ -C ₄₀	Asphalt	3.4	3.3
	—	Other products	6.0	3.0

is done in practically all refineries; it is a commercial success due to cheapness of the high boiling variety. About 50% of our gasoline is thus made. The yield may be as high as 85% under suitable conditions. Catalytic cracking gives a gasoline with better 'anti-knock' value as the straight-chain alkanes in petroleum are thus partly converted into branched-chain compounds of higher octane number (p. 54). During cracking, unsaturated hydrocarbons (e.g., ethylene) are formed in large amounts. These are polymerised into liquid and used as motor fuel. The process consists in heating the gases, preferably under pressure, in presence of catalysts like phosphoric acid. In U.S.A. the annual production of petrol from this source has been estimated at over 100 million barrels; synthetic rubber is made from cracked gases there.

By passing straight-run gasoline under pressure (400-750 p.s.i.) *rapidly* over a catalyst such as alumina or molybdena in steel pipes heated to about 600°, the octane number of the fuel is often increased by 10-20 units. The process, called *reforming*, involves the conversion of straight-chain paraffins into branched-chain paraffins and aromatic hydrocarbons which have a higher octane number. The yield of cracked gasoline lies between 60-90%. The percentage composition of straight-run and cracked gasoline is given below:

	Unsaturated hydrocarbons	Aromatics	Paraffins	Naphthenes
Straight-run	1.4	4.9	69.8	23.7
Cracked	10.9	19.8	51.3	18.0

The fuel consumption by an engine rises rather rapidly as the octane number falls; thus the consumption of gasoline with octane number

100 is 230 c.c. per H.P. per hour, but it is 325 c.c. when the octane number is 73.

Laboratory gas for burners is generally made by cracking crude oil in places where coal gas is not available—this is usually done by dropping the oil on a red-hot metallic plate. On a small scale, it may be obtained by blowing air through aviation spirit or cheaper solvent oil.

Shale oil.—A bituminous shale, found in Scotland and U.S.A., yields on destructive distillation an oil which after purification is fractionated into naphtha, paraffin oil, light mineral oil and waxy residue. Shale oil has a lower calorific value than petroleum.

Synthetic motor fuels.—The great demand for gasoline has led to the development of methods for the synthesis of hydrocarbons from coal in countries having little or no natural petroleum. Coal is a complex mixture of high-molecular organic compounds and elementary carbon. In the **Bergius process**, low grade powdered coal in the form of a paste with heavy oil (1:1) at 450° is hydrogenated by pure hydrogen at 250 atmospheres, when mixtures of low-boiling hydrocarbons are formed. The method has since been modified by the use of catalysts such as hydrated iron oxide, and replacing hydrogen by water-gas. There are several plants in Germany producing appreciable quantities of synthetic petrol. The plant at Billingham, England, which closed down in 1958 after 23 years, was capable of producing annually 30 million gallons of motor fuel from coal. In the **Fischer-Tropsch process**, developed in Germany between 1925-36, liquid hydrocarbons (synthetic petrol) are produced by passing a mixture of purified H_2 and CO (in the ratio 2:1) over catalysts (usually cobalt with thoria as promoter mounted on kieselguhr) under a pressure of 5-15 atmospheres at 190-200°. The yield is nearly 66% of the theoretical. Metal carbides are first formed between water-gas ($CO + H_2$) and metals (Co, Ni or Fe) with subsequent reduction by hydrogen to methylene radicals. The latter then polymerise to higher hydrocarbons which are fully hydrogenated to saturated compounds. Unlike the Bergius process, it can be operated economically on a small scale. As oil resources of the world are likely to be exhausted much earlier than coal deposits, the hydrogenation of coal goes a long way in solving the petrol problem. The estimate of proved petroleum resources of the world on January 1, 1936, was 21965×10^6 barrels of which 10575×10^6 barrels were in U.S.A. and only 111×10^6 barrels in India and Burma together.

In 1955-56 India imported 233,802,048 gallons of kerosene valued at Rs. 19,52,64,531 and 296,430,736 gallons of other mineral oils worth Rs. 8,96,60,019. She also imported in the same year 73,078,496 gallons of motor spirit valued at Rs. 9,07,80,229. Two refineries for crude oil are operating in India; their capacity is 3.7 million tons a year. The coal resources of India have got to be utilised to make her largely independent of foreign supply of mineral oils.

The normal straight-chain hydrocarbons of gasoline knock badly in a high compression engine (the petrol-air mixture burns with explosion in the cylinders causing a metallic rattling) much power and engine efficiency are thus lost. Knocking also increases wear on the engine. Anti-knock compounds like lead tetraethyl are added to ordinary gasoline to overcome this. Branched-chain hydrocarbons (e.g., isopentane and cycloparaffins knock only under extreme conditions. 2,2,4-trimethyl-pentane (wrongly called iso-octane) has been chosen as the standard anti-knock fuel and given an octane number of 100, and *n*-heptane which knocks very readily, one of 0.

The octane number of a fuel is the p.c. of iso-octane that has to be added to *n*-heptane to produce the same knocking as the fuel itself does in a standard engine under definite conditions. Straight-run gasolines may have any octane number between 20 and 73. Gasoline of high octane number and anti-knock

compounds, e.g. lead tetraethyl, have recently made high compression engines work smoothly in motor cars resulting in about 33% economy in fuel.

Petrochemicals.—Natural gas and petroleum are no doubt very important sources for heat, light and mechanical energy; these are in recent years supplying increasing quantities of various synthetic organic chemicals directly or indirectly. For example, methyl chloride, formaldehyde, methanol, chloroform, etc. are made from methane; ethanol, ethylbenzene, butadiene, styrene, glycol from ethylene; isopropyl alcohol, acetone, diketene, acetic anhydride, ethanol, glycerol from propylene; nitromethane, nitroethane and nitropropanes from propane; butyl alcohols and butadiene from butylene; amyl alcohols from amylenes; benzene from *n*-hexane and toluene from heptane. Some 200 organic chemicals are now derived from petroleum and natural gas. U.S.A. thus makes over 500 million lb. each of methanol, ethanol, 2-propanol, glycol and styrene per year; about 25% of the industrial chemicals in U.S.A. come from this source.

QUESTIONS

1. What are paraffins? Why are they so called? Give the general methods for their preparation.

2. Give an account of the petroleum industry, indicating the use to which different products are put. (Punjab Inter., 1931).

4. Explain the terms with illustration: (i) homologous series, (ii) alkyl radical, (iii) substitution, (iv) additive product, (v) polymerisation.

5. What do you understand by isomerism? Discuss isomerism in the paraffin series of hydrocarbons. Give all the possible isomers of the hydrocarbon, C_6H_{14} .

6. Why special interest is attached to aliphatic hydrocarbons, and specially to methane, in a discussion of organic chemistry?

7. Name some important substances obtainable today from natural petroleum. From what other sources, and how, is petroleum obtainable? What is a petrol substitute and why is it needed? (B.Sc. Exam. 1947, Benares Hindu Uni.).

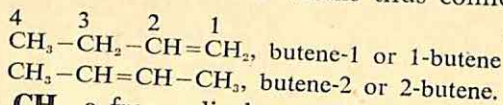
CHAPTER VI

THE UNSATURATED HYDROCARBONS

Hydrocarbons having less hydrogen than the corresponding paraffins are the **unsaturated hydrocarbons**, represented by C_nH_{2n} , C_nH_{2n-2} , C_nH_{2n-4} , C_nH_{2n-6} , etc. The most notable of these are the **olefines** or **alkenes**, C_nH_{2n} , and the **acetylenes** or **alkynes**, C_nH_{2n-2} . The olefines have two hydrogen atoms less than the corresponding paraffins. The functional group in the alkenes is $-C=C-$. Some important plant products *e.g.*, rubber and carotene (orange pigment of carrots) are olefinic compounds. Their names are derived from the alkyl groups by adding the suffix '—ene', or from the paraffins by changing '—ane' into '—ene':

Paraffin	Radical	Olefine
C_2H_6	$-C_2H_5$	C_2H_4
Ethane	Ethyl	Ethylene or ethene
C_4H_{10}	$-C_4H_9$	C_4H_8
Butane	Butyl	Butylene or butene

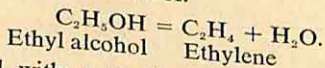
The position of the double bond is indicated by affixing or prefixing the lower number of the two carbon atoms thus connected *e.g.*,



Methylene, CH_2 , a free radical, may be obtained by heating diazomethane, CH_2N_2 , mixed with ether or butane, between 350° - 600° at a low pressure; nitrogen is thus split off. The life period of methylene is only a fraction of a second. Methylene removes the mirror of arsenic or antimony from a glass tube through which it passes. It readily forms ethylene, and reacts with hydrogen at 300° to give methane.

Ethylene, C_2H_4 , is present in coal gas (3-4% by volume) and makes the flame luminous. The gas from the low temperature production of coke contains about 6% of it. American natural gas has a fairly high proportion (up to 20%) of ethylene. It also results in large quantities during cracking (p. 53). Ethylene was first made in 1795 by five Dutch chemists from spirit of wine and oil of vitriol. With chlorine, ethylene gave ethylene dichloride, an oily liquid which they called Dutch liquid. Hence ethylene was named olefiant or oil-forming gas (Latin *oleum* oil, *fio* to make). The term 'olefines' represents ethylene and its homologues.

Preparation.—It is prepared in the laboratory by heating ethyl alcohol with excess of concentrated sulphuric acid, or better, with syrupy phosphoric acid, both, being strong dehydrating agents, abstract the elements of water from the alcohol.



A litre-flask, fitted with a tap-funnel and a thermometer, is placed on a sand-bath. The delivery tube is connected to wash-bottles containing strong

caustic potash and the latter to an inverted gas jar filled with water. 50 c.c. of 95% ethyl alcohol mixed with 100 c.c. of concentrated sulphuric acid are taken in the flask and also about 8 g. of anhydrous aluminium sulphate to

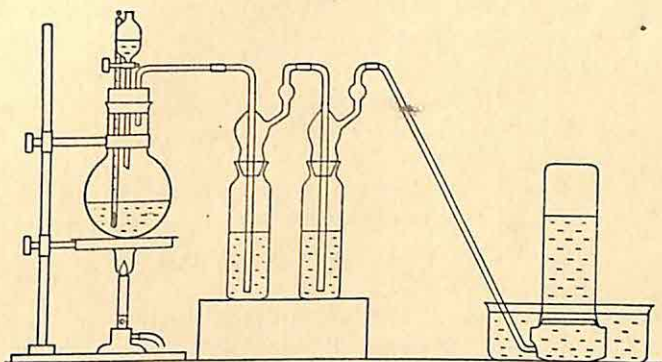
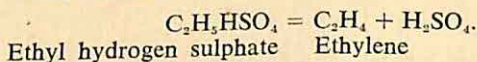
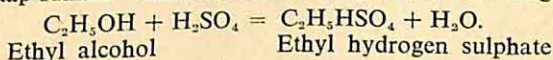


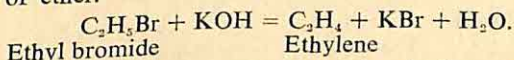
Fig. 21. Preparation of ethylene.

prevent frothing and for better yield of ethylene. The thermometer dips into the liquid. The temperature is gradually raised and at about 165° , ethylene issues out together with a little carbon dioxide, sulphur dioxide, etc. These are absorbed by caustic potash. When the evolution of gas slackens, a fresh mixture of ethyl alcohol and sulphuric acid (1:1 by volume) is added slowly through the tap-funnel. The reaction takes place in two stages:

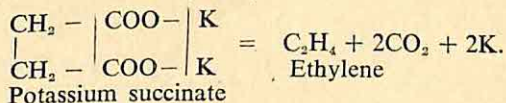


Theoretically, there should be no loss of H_2SO_4 , but in actual practice, a portion of the acid is reduced by ethylene. Some carbon monoxide is also produced from the alcohol by the oxidising action of H_2SO_4 . The acid must always be in *excess* otherwise, we get ether, $\text{C}_2\text{H}_5\text{-O-C}_2\text{H}_5$, and little ethylene. A purer product, in better yield, is obtained with syrupy phosphoric acid at about 200° , the alcohol is slowly run down. Troublesome frothing is also avoided.

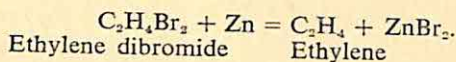
(ii) Ethylene is formed by the action of hot and strong alcoholic solution of caustic potash on ethyl bromide or iodide; potash removes a molecule of halogen acid from the alkyl halide. But the yield is less than 1% due to the formation of ether.



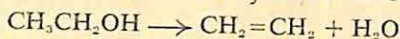
(iii) Electrolysis of a concentrated solution of potassium succinate yields ethylene and carbon dioxide at the anode (*cf.*, preparation of ethane from sodium acetate, p. 44).



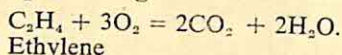
(iv) Pure ethylene may be obtained by warming ethylene dibromide in alcohol with granulated zinc, or by dropping the dibromide into a suspension of zinc dust in alcohol and glacial acetic acid.



(v) By passing alcohol vapour through an iron tube packed with alumina or pumice stone soaked in syrupy phosphoric acid at about 360°, ethylene is manufactured. The yield is about 98%.

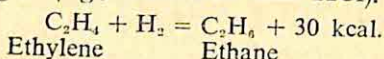


Properties.—Ethylene is a colourless gas with a faint sweetish odour. It is sparingly soluble in water but more soluble in alcohol or ether. It produces anæsthesia on inhalation and burns with a luminous flame in air, producing carbon dioxide and water.

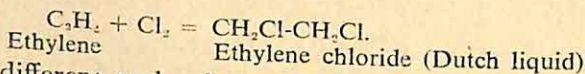


Ethylene forms an explosive mixture with air or oxygen. Chemically, unlike the paraffins, it is reactive due to unsaturation. Ethylene is quantitatively absorbed by concentrated AgNO_3 solution from which it can be recovered by evacuation. At about 300° and 1500 atmospheres ethylene forms linear thermoplastic polymers, polyethylenes or *polythenes* (*vide* p. 68 reaction (9)). Traces of oxygen catalyses the reaction. These are tough, flexible plastics. U.S.A. made 400 million lb. in 1955.

Reactions.—(i) In presence of palladium or platinum black at ordinary temperature, or finely divided nickel at 150°, ethylene and hydrogen form ethane quantitatively. Olefines *cannot* be hydrogenated with nascent hydrogen (*e.g.*, from zinc and HCl).

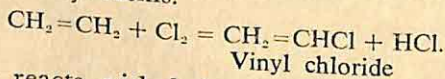


(ii) Ethylene combines with chlorine, bromine and iodine in carbon tetrachloride solution, forming addition compounds, most readily with chlorine and least so with iodine. Iodine monochloride, ICl , in carbon tetrachloride readily adds to an ethylenic bond, giving a 'mixed' halogen compound.

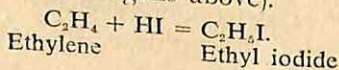


When two different molecules unite directly and no part of either separates out, the reaction is called an *addition reaction* and the product, an *additive product*.

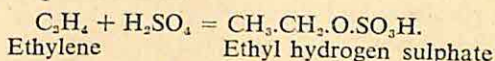
Heated with chlorine at 350-450°, ethylene forms vinyl chloride which is made into vinyl resins.



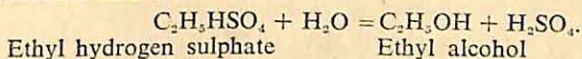
(iii) Ethylene reacts with halogen acids in strong aqueous solutions, forming alkyl halides at 100°. It reacts most readily with hydriodic acid and least so with hydrochloric acid. In presence of bismuth trichloride, BiCl_3 , however, the reaction with HCl is quite rapid (*cf.* the reactions with halogens above).



(iv) Concentrated sulphuric acid readily absorbs ethylene under pressure at 85° forming ethyl hydrogen sulphate or ethyl sulphuric acid. The olefines may thus be separated from gases which do not react with strong sulphuric acid.



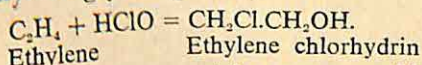
Ethyl hydrogen sulphate suffers hydrolysis on boiling with 50% H_2SO_4 giving alcohol and a little ether.



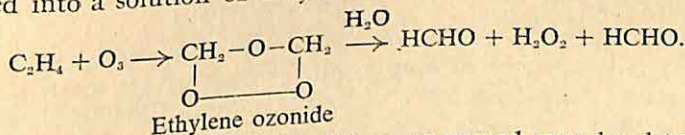
The ethylene of coal gas may thus be converted into alcohol. It is not yet a commercial process owing to higher cost of production, though one ton of coal would give about $1\frac{1}{2}$ gallons of alcohol. But ethylene from natural gas and cracking is thus made into alcohol in U. S. A. By passing steam and ethylene under high pressure at 300° over tungsten oxide, ethyl alcohol is made commercially in U. S. A. by direct hydration :



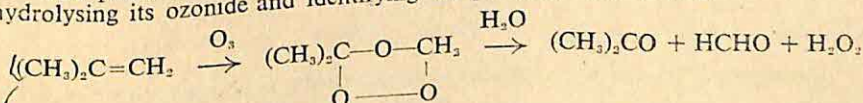
(v) With hypochlorous acid, HClO , ethylene forms ethylene chlorhydrin, a colourless liquid; ethylene and carbon dioxide may be passed into a suspension of bleaching powder in water. The chlorhydrin is used in making ethylene glycol (p. 108).



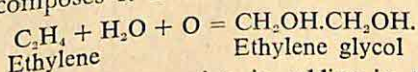
(vi) Ethylene unites with ozone giving an unstable *ozonide* which decomposes, on warming with dilute acids or heating with water, into hydrogen peroxide, H_2O_2 , and formaldehyde, HCHO . The former oxidises the latter to formic acid, HCOOH . Ozonised air or oxygen is passed into a solution of ethylene in a nonaqueous solvent.



The position of the double bond in a compound may be determined by hydrolysing its ozonide and identifying the products thus formed.



(vii) A dilute, alkaline solution of potassium permanganate, KMnO_4 , in water oxidises ethylene to glycol *in the cold*; a concentrated solution decomposes it to carbon dioxide and water.



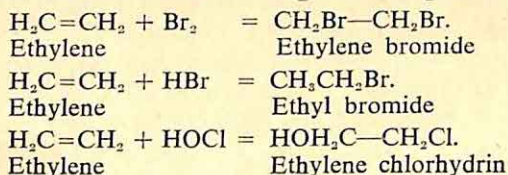
Baeyer test for unsaturation consists in adding in the cold 1-2 drops of 1% KMnO_4 solution, made alkaline with Na_2CO_3 solution, to an alcoholic solution of the compound. The colour disappears rapidly if it is unsaturated. Other compounds such as aldehydes reduce KMnO_4 solution, but slowly. Ethylenes can thus be distinguished from isomeric cycloparaffins (p. 63) which are saturated. The test is not obviously specific for a double bond.

Uses.—Ethylene is used for making alcohol, mustard gas and preserving and artificial ripening of green fruits. In presence of

1 part of ethylene in 1000 parts of air, green fruits 'ripen' rapidly. It stimulates the growth of potatoes. With 20% oxygen it is an anæsthetic. Trichloro-ethylene is a fat solvent. *Thiokol*, a synthetic rubber, is made by reacting ethylene chloride with Na_2S_4 . Polythene plastics are chemically inert, translucent and good electric insulators. Some laboratory wares and bottles are made from it; they are unbreakable.

Production of **Alkathene** (I.C.I. brand of polythene) started with an annual capacity of 3500 tons near Calcutta in 1959; ethylene is made from alcohol of sugar factories. India consumed 2100 tons of polythene in 1958.

The structure of ethylene.—From analytical data, ethylene is C_2H_4 . By catalytic hydrogenation, it yields ethane. This and its formation from ethyl alcohol show that ethylene has two carbon atoms linked directly. It is either (i) $\text{H}_2\text{C}-\text{CH}_2$ or (ii) $\text{H}_3\text{C}-\text{CH}$. With bromine ethylene yields ethylene dibromide, $\text{C}_2\text{H}_4\text{Br}_2$, which is isomeric with ethylidene bromide, $\text{H}_3\text{C}-\text{CHBr}_2$, obtained from acetaldehyde, CH_3CHO , by replacing the oxygen with two atoms of bromine. Hence ethylene dibromide is $\text{CH}_2\text{Br}-\text{CH}_2\text{Br}$ and ethylene, $\text{CH}_2=\text{CH}_2$. With normal valency, ethylene is either $-\text{CH}_2-\text{CH}_2-$ or $\text{H}_2\text{C}=\text{CH}_2$. The latter is correct, free radicals such as $-\text{CH}_2-$ and $-\text{CH}_3$ being extremely unstable. The double bond, called **ethylene linkage**, means that all the covalencies of carbon have not been properly satisfied. This explains the addition of halogens, halogen acids, etc. by ethylene:



Thus ethylene invariably combines with *two* univalent atoms or groups. It is impossible to satisfy the valency of one carbon without simultaneously satisfying that of the other. Two carbon atoms with unsatisfied valencies are always adjacent, a structure like $\text{H}_3\text{C}-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_3$, being unknown. * These facts go against the

existence of free valence.

Compared to ethane, ethylene is far more reactive; the reactivity

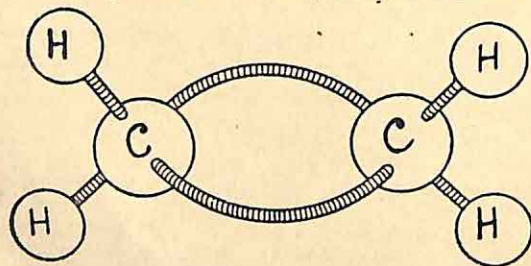


Fig. 22. Double (ethylene) linkage.

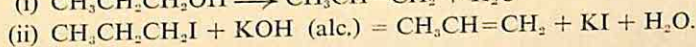
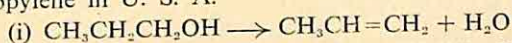
is generally attributed to its instability. Adolf von Baeyer, a German chemist, tried to explain this instability of the double bond by his **strain theory** and considered ethylene as a 2-membered ring. The four valence bonds of carbon are, according to van't Hoff, projected towards the four apexes of a regular tetrahedron—the atom itself being at the centre (Fig. 18f). The angle

tetrahedron—the atom itself being at the centre (Fig. 18f). The angle

between any two bonds is $109^{\circ} 28'$ which is maintained when carbon atoms are linked with single bonds; in such cases no strain is produced. In a double bond, the valencies are considerably 'displaced' from their normal position (Fig. 22). This causes certain strain in the molecule according to Baeyer. As a result, the compound becomes unstable. An unsaturated compound thus tends to pass to the saturated state by addition reaction.

But a double bond between C atoms is thermodynamically more stable than a single bond as more heat energy (145 kg.cal./mole) is necessary to break the double bond in ethylene than to break a single bond in methane (which requires only 81.1 kg.cal./mole). For a triple bond in acetylene, it is 190 kg.cal./mole. So physically, a triple bond is more stable than a double bond and a double bond more stable than a single. Resistance to stretching and compression is also correspondingly higher for a triple bond than for a double or single bond. A multiple bond pulls the carbon atoms closer together than a single bond; thus the interatomic distances between C-C, C=C and C $\equiv$ C are respectively 1.54Å, 1.34Å and 1.20Å (1Å = 10^{-8} cm.).

Propylene, propene, CH₃CH=CH₂, is obtained as a by-product in huge quantity during cracking of petroleum. It may be prepared by heating (i) propyl (or iso-propyl) alcohol with H₂SO₄, or (ii) *n*-propyl iodide with alcoholic KOH. It is a colourless gas, insoluble in water but soluble in alcohol like ethylene, and more reactive. Isopropyl alcohol, acetone, glycerine, etc. are manufactured from propylene in U. S. A.

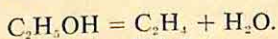
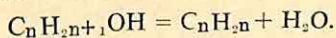


Butylenes, butenes, C₄H₈, exist in three isomeric forms, all are found in the gases from cracked petroleum. Butene-1 or α -butylene, CH₃CH₂CH=CH₂, may be prepared from *n*-butyl alcohol, CH₃CH₂CH₂CH₂OH, and H₂SO₄; some butene-2 or β -butylene, CH₃CH=CHCH₃, is also formed. Iso-butylene or γ -butylene, (CH₃)₂C=CH₂, may be obtained from isobutyl alcohol, (CH₃)₂CH-CH₂OH, and H₂SO₄. The butylenes resemble propylene but polymerise (p. 68) more readily than the lower olefines. Isobutylene is quite stable, it gives with chlorine mainly a substitution product, ClCH₂(CH₃)C=CH₂. 1- and 2-butene are used largely for making secondary butyl alcohol, and isobutylene for tertiary butyl alcohol, both alcohols are industrial solvents. Iso-octane is made from isobutylene. 2-Butene exhibits cis-trans isomerism (p. 250) and has two forms.

The olefines, C_nH_{2n}.

Name	Formula	B.P.
Ethylene, C ₂ H ₄	CH ₂ =CH ₂	-103°
Propylene, C ₃ H ₆	CH ₃ -CH=CH ₂	-48°
<i>n</i> -Butylene, C ₄ H ₈	CH ₃ -CH ₂ -CH=CH ₂	-5°
Isobutylene, C ₄ H ₈	CH ₃ -CH=CH-CH ₃	-6°
<i>n</i> -Amylene, C ₅ H ₁₀	CH ₃ -(CH ₂) ₂ -CH=CH ₂	40°
<i>n</i> -Hexylene, C ₆ H ₁₂	CH ₃ -(CH ₂) ₃ -CH=CH ₂	64°

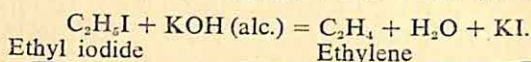
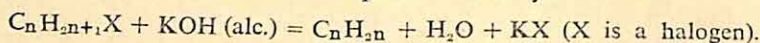
General methods of preparation.—(1) By the action of strong dehydrating agents *e.g.*, conc. sulphuric acid, zinc chloride, syrupy phosphoric acid, etc., on alcohols:



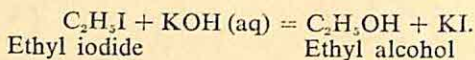
Ethyl alcohol Ethylene

By passing alcohol vapour through a tube packed with alumina, Al_2O_3 , at 360° , the corresponding olefine is obtained in good yield.

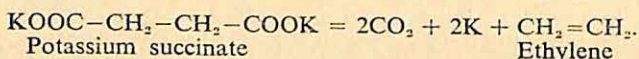
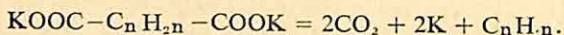
(2) By the action of alcoholic potash on alkyl halides:



Aqueous potash, however, gives an alcohol instead of an olefine.

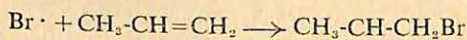


(3) By the electrolysis of sodium or potassium salts of dibasic acids of the succinic acid series:



General properties.—The first four members are gases; the higher ones are liquid and solid at ordinary temperature. They are colourless. Physically, they resemble the paraffins; there is a similar gradation of properties with rise in molecular weight, in respect of density, m.p., b.p., etc. The olefines are practically insoluble in water, but soluble in alcohol, ether, etc.

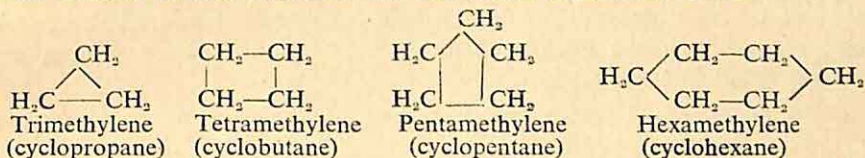
The other olefines behave like ethylene. Thus they burn with a luminous, smoky flame and form explosive mixtures with air or oxygen. They also readily combine with halogens, halogen acids, etc. to form additive compounds. When an olefine having unequal number of hydrogen atoms between unsaturated C-atoms, combines with halogen acids, the hydrogen of the halogen acid usually goes to the carbon richer in hydrogen. Thus propylene, $\text{CH}_3-\text{CH}=\text{CH}_2$, and HBr give mainly iso-propyl bromide or 2-bromo-propane, $\text{CH}_3\text{CHBrCH}_3$, and only traces of normal propyl bromide, $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$, with pure reagents and in absence of air. This is *Markownikoff's Rule* (1869) which applies only to olefines; there are, however, exceptions. The addition of water also takes place likewise. Thus propylene, $\text{CH}_3-\text{CH}=\text{CH}_2$, gives mainly isopropyl alcohol, $\text{CH}_3\text{CHOHCH}_3$. In presence of oxygen, ultraviolet light or peroxides, however, HBr adds to propylene much more quickly and against *Markownikoff's Rule*, $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ being formed. Atomic bromine, set free by peroxide, reacts with propylene giving a free radical and a chain reaction follows:



Addition or substitution occurs, depending upon conditions, when Cl_2 or Br_2 reacts with an olefine; thus in a solvent at low temperature, Cl_2 and propylene yield mainly propylene chloride, $\text{CH}_3-\text{CHCl}-\text{CH}_2\text{Cl}$, but allyl chloride $\text{ClCH}_2-\text{CH}=\text{CH}_2$, predominates at 400° (vide vinyl chloride, p. 58).

The olefines give paraffins on catalytic hydrogenation. They are oxidised by alkaline potassium permanganate or bromine-water. The decolorisation of bromine-water or dilute potassium permanganate solution (p. 59) serves as a test for the olefines, or more generally, for unsaturation. Fuming sulphuric acid, ozone, etc., react with other olefines as with ethylene.

Cycloparaffins.—Isomeric with the olefines are the saturated hydrocarbons, polymethylenes or cycloparaffins (vide Chapter XXX). They have a ring structure, and resemble the paraffins but the lower members behave somewhat like the olefines. They are less reactive, and having no double bond, form no additive compounds. Of the first four members, cyclopentane and cyclohexane, found in some natural petroleum, are also called naphthenes (p. 52).



Diolefines, $\text{C}_n\text{H}_{2n-2}$, have two double bonds. The most important are isoprene, $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2$, and 1,3-butadiene, $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$. A hydrocarbon with two double bonds is known as diene. Isoprene (b.p. 34°) was originally obtained by the dry distillation of natural rubber, it is now made from isoamyl alcohol. Rubber, mainly a hydrocarbon of high molecular weight, $(\text{C}_5\text{H}_8)_n$, is obtained by coagulating the sap (called latex) of the rubber tree. Isoprene and butadiene polymerise in presence of metallic sodium or on prolonged heating to 70° and yield a product resembling rubber. U.S.A. makes butadiene by catalytic dehydrogenation of butane obtained from natural gas or cracking of petroleum.

During the war of 1914-18, the Germans got no rubber from the Far East and made it from dimethyl butadiene, $\text{CH}_2=\text{C}(\text{CH}_3)-\text{C}(\text{CH}_3)=\text{CH}_2$, obtained from acetone. In the last war also, Germany met 2/3 of her requirements from synthetic rubber 'Buna' (from Butadiene and Natrium, i.e., sodium). The method was discovered by chance in an attempt to dry a sample of isoprene with metallic sodium. Natural rubber is vulcanized into various non-adhesive substances of higher flexibility and elasticity before use—vulcanization (discovered by Charles Goodyear, an American, in 1839), consists essentially in heating raw rubber with sulphur (5-7%) or some sulphur compounds in presence of accelerators to about 140° . Fillers like carbon, silica, Sb_2S_3 , BaSO_4 , ZnO , gypsum, etc., are added to prolong the life and also to impart colour. Goodyear accidentally threw some raw rubber and sulphur on a hot stove and obtained a remarkably changed product.

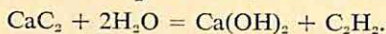
Since 1932 a new synthetic rubber, neoprene, is being manufactured in U.S.A. from vinyl acetylene, $\text{CH}\equiv\text{C}-\text{CH}=\text{CH}_2$ (made from acetylene) by converting it into chloroprene, $\text{CH}_2=\text{CCl}-\text{CH}=\text{CH}_2$, which spontaneously polymerises to rubber. Its oil resistance counterbalances its higher cost. U.S.A. made 1,130,000 tons of synthetic rubber in 1955 from chloroprene, styrene and butadiene. The price was 22 to 42 cents per lb. compared to 30 cents for natural rubber in 1955. Synthetic rubber is also made in Soviet Russia (Sovprene) and Japan (Hitakol). U.S.A. started large scale manufacture of synthetic rubber after the occupation of Malaya, East Indies, etc. by Japan in 1942. World production of crude rubber in 1955 was 2 million tons. U.S.A. normally consumes about half the world production.

The acetylenes, alkynes, $\text{C}_n\text{H}_{2n-2}$, are more unsaturated than the olefines, having two hydrogen atoms less. From the first member, acetylene, the name of the series is derived. But the nomenclature is

unsystematic; they are usually named as alkyl derivatives of acetylene, e.g., methyl acetylene, $\text{CH}_3-\text{C}\equiv\text{CH}$, etc. Systematic names from the corresponding paraffins by substituting '-an' with '-ine' are not widely used; e.g., acetylene is ethine, the next, propine and so on. Some have special names—e.g., propine, C_3H_4 , is better known as allylene, and butine, C_4H_6 , as crotylene.

Acetylene, C_2H_2 , does not occur in nature; coal gas contains traces of it (about 0.06% by volume). It is formed during incomplete combustion of coal gas (e.g., when a Bunsen flame strikes back), ethyl alcohol, hydrocarbons, etc. It was discovered by accident in 1892. In an attempt to obtain metallic calcium, Wilson, an American, heated a mixture of coke and lime in an electric furnace and poured the resulting grey mass into a bucket of water. A copious supply of acetylene was obtained but no calcium.

Preparation.—(1) Acetylene is generally made by the action of water on calcium carbide, CaC_2 , a hard, black solid.



The bottom of a conical flask is covered with a layer of sand and some small lumps of calcium carbide are then added. Water is dropped from the tap-funnel and the liberated gas collected over water. Acetylene thus prepared has traces of arsine, phosphine, etc. The foul odour of acetylene burners is due to the presence of phosphine (calcium phosphide, Ca_3P_2 , present in carbide gives phosphine with water). pure acetylene has a sweetish smell. The gas often contains traces of H_2S and NH_3 , which may be removed by passing it through an acidified solution of copper sulphate. Carbide is manufactured by heating a mixture of coke and lime at $2500^\circ\text{--}3000^\circ$ in a closed electric furnace. The product contains about 85% CaC_2 .

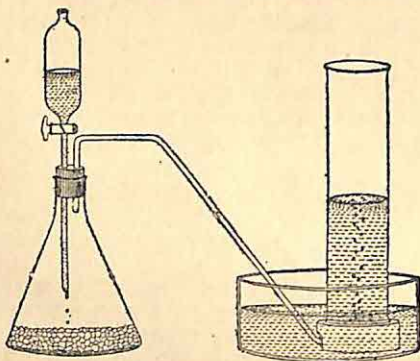
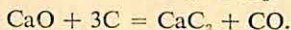
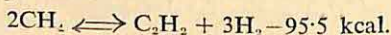


Fig. 23. Preparation of Acetylene.

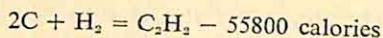


Acetylene is thus obtained from carbon. This is a complete synthesis, because both carbide and water can be made from their elements. Acetylene can be converted into various organic compounds by different reactions. Their formation may also be regarded as synthesis from elements. In 1957 India produced 3,596 tons of CaC_2 but consumed 13,000 tons; during 1956-57, 5,976.35 tons were imported, valued at Rs. 37.29 lacs. High cost of electric power is a handicap to the Indian industry.

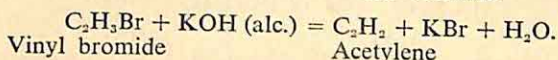
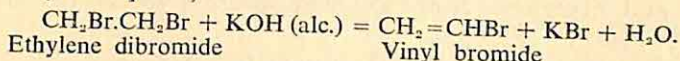
The method is cheap and followed commercially. By electric arc cracking process, methane (natural gas), coke oven gas, etc. give acetylene in good yield. Germany thus makes acetylene from coal gas. In U.S.A. acetylene in fairly high yield is obtained by exposing natural gas to $1400\text{--}1600^\circ$ for 0.1–0.01 second and cooling the products suddenly by spraying water.



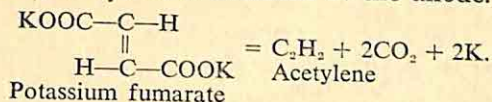
(2) Acetylene may be made from its elements by striking an electric arc between carbon poles in an atmosphere of hydrogen. The yield is only 3.7% at 2500°.



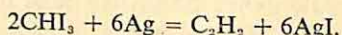
(3) By heating ethylene dibromide (or ethylidene dibromide, CH_3CHBr_2), with alcoholic potash, acetylene is obtained (*cf.*, preparation of ethylene, p. 57).



(4) On electrolysis of a strong, aqueous solution of potassium salt of fumaric or maleic acid (*cf.*, preparation of ethane, p. 44, and of ethylene, p. 57), acetylene is obtained at the anode.

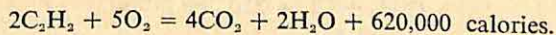


(5) Heated with silver powder, iodoform, CHI_3 , gives acetylene:



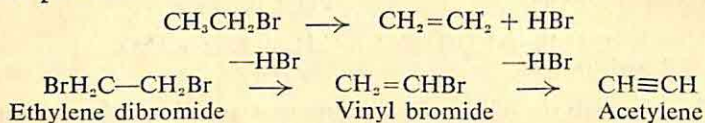
Properties.—Acetylene, a colourless gas, has a pleasant odour when pure. It condenses to a highly explosive liquid (b.p. -84°). It is illegal to store or use liquid acetylene. Above 2 atmos., the gas explodes. Acetone dissolves about 300 times its volume of acetylene at 12 atmospheres and 15°. Commercially, acetylene is stored under pressure in steel cylinders packed with porous briquettes soaked in acetone. When the pressure is released, acetylene comes out with little loss of acetone. Water dissolves its own volume of acetylene at 0° and 76 cm. pressure.

Like ethane and ethylene, acetylene mixed with air or oxygen in certain proportions, explodes when ignited. The gas burns in air with a smoky flame due to incomplete combustion, but in specially constructed, pin-hole burners, exposing a large surface of the flame to the air, the gas produces a dazzling and almost smokeless flame. These are used in country houses. The illuminating power of acetylene is nearly 15 times that of coal gas. When acetylene burns in oxygen, the oxy-acetylene flame attains a temperature of about 3500°, at which practically all metals melt.

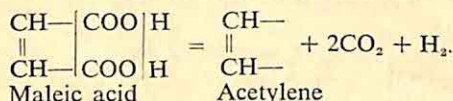


This is utilised in welding and cutting metals. The proportion of oxygen and acetylene is so adjusted that carbon monoxide is produced, which reduces any oxide film formed during welding. In cutting metals, an excess of oxygen is supplied so that the metal burns. Like ethylene, acetylene is also used for ripening fruits.

Structure of acetylene.—From analytical data, the acetylene molecule is C_2H_2 . Its formation from ethylene dibromide, or maleic and fumaric acid salts shows that the two atoms of carbon are directly linked. Therefore, acetylene is either CH_2-C , or $CH-CH$. Now, in the removal of halogen hydracid from alkyl or alkylene halides, hydrogen, as a rule, comes from one carbon atom and halogen from the adjoining one. Ethylene is thus formed from ethyl bromide, and acetylene from ethylene dibromide by the action of alcoholic potash:



Maleic acid, on electrolysis, gives acetylene:



With normal valency and no free bond, acetylene should, therefore, be $CH\equiv CH$. The triple bond indicates a still greater strain in the valency bonds between the carbon atoms (*vide* p. 60).

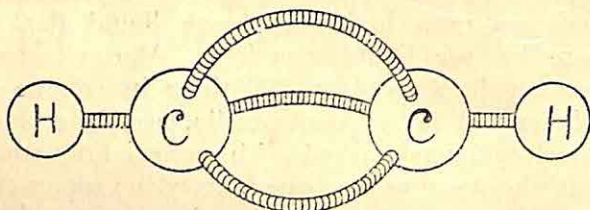
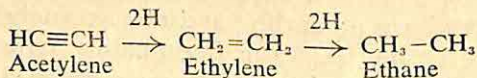
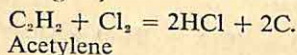


Fig. 24. Triple (acetylene) linkage.

Reactions.—(1) On hydrogenation in presence of finely divided nickel at 100° , or platinum black at ordinary temperature, acetylene gives ethylene and then ethane.



(2) Acetylene and chlorine combine at room temperature with explosive violence, producing hydrochloric acid and carbon:

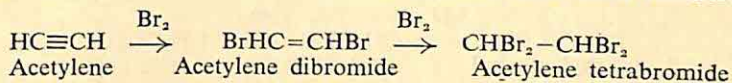


In presence of a solvent or kieselguhr, no explosion occurs, an additive compound, acetylene tetrachloride, $C_2H_2Cl_4$, is formed:

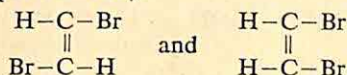


It is a non-inflammable liquid (commercially known as 'Westron') employed as a solvent for rubber, fats, varnishes, etc. and also as an insecticide. By passing westron over heated barium chloride, HCl is lost and trichloroethylene, $\text{CCl}_2=\text{CHCl}$, is obtained. It is called 'Westrosol' and used for dry cleaning and extracting oils from seeds.

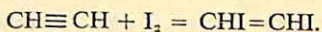
(3) With acetylene, bromine reacts much less vigorously than chlorine. Acetylene dibromide is first formed and then tetrabromide.



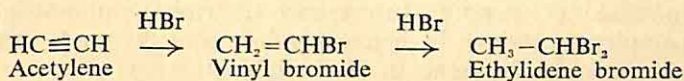
Two isomeric dibromides are known having different graphical formulae (see Chapter XXIV):



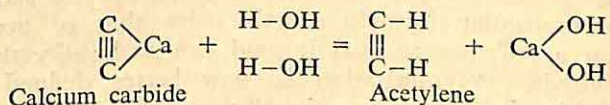
Acetylene slowly adds on iodine in ethyl alcohol to give acetylene di-iodide:



(4) With hydrobromic acid, it very slowly forms vinyl bromide and then ethylidene bromide; a mercuric halide accelerates the reaction. The halogen goes to the carbon poorer in hydrogen, following Markownikoff's rule (p. 62). With hydriodic acid, similar products are obtained.



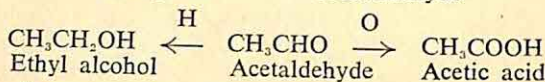
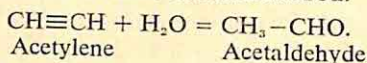
(5) Unlike ethylene, acetylene forms metallic derivatives called *acetylides*, the hydrogen atoms being replaced by metals. When acetylene is passed through an ammoniacal solution of silver or copper salt, the corresponding acetylide, Ag_2C_2 or Cu_2C_2 is formed. These are highly explosive when dry. But war-time developments in Germany have shown that acetylene can be safely used under pressure (by diluting acetylene with an inert gas, e.g., N_2), and copper acetylide employed as a catalyst in some reactions. With ammoniacal solution of cuprous chloride, traces of acetylene can be detected, a red ppt. or coloration due to copper acetylide results. The copper or silver compound gives acetylene with dilute hydrochloric acid or warm potassium cyanide solution. Pure acetylene is thus obtained. Acetylides (or carbides) of alkali and alkaline earth metals are more stable, and yield acetylene with water.



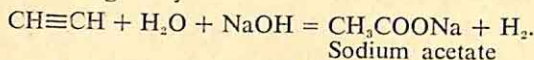
The H of the terminal C in 1-alkynes is weakly acidic, being sufficiently positive for heterolysis of the bond, by the removal of a proton, to occur. Methyl acetylene, $\text{CH}_3-\text{C}\equiv\text{CH}$, gives the silver salt, $\text{CH}_3-\text{C}\equiv\text{CAg}$, but not dimethyl acetylene, $\text{CH}_3\text{C}\equiv\text{CCH}_3$.

(6) When acetylene is passed through rapidly agitated 20% sulphuric acid at 80° in presence of about 1% mercuric sulphate,

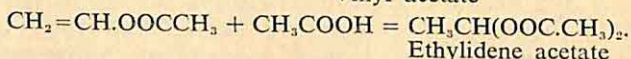
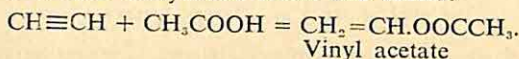
acetaldehyde is obtained; this, on catalytic reduction, gives ethyl alcohol, and on oxidation with air in presence of manganese acetate, acetic acid—two very important products. Where electricity is cheap for making CaC_2 , ethyl alcohol is thus manufactured.



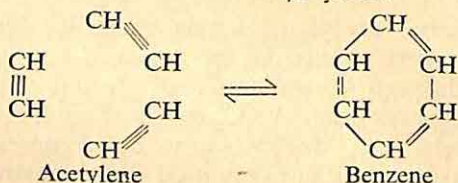
(7) By passing acetylene and steam into caustic soda at 220° , we get sodium acetate in good yield:



(8) Acetylene, led into acetic acid in presence of mercuric salts at 80° , gives vinyl acetate and ethylidene acetate. Plastics are made from the former, and acetic anhydride from the latter.



(9) Passed through a tube at about 400° , three acetylene molecules coalesce to form benzene and other aromatic hydrocarbons; it is not a good way of making benzene. In presence of triphenylphosphine-nickel carbonyl complex, acetylene in benzene solution at 60° under 15 atmospheres pressure forms benzene in 90% yield.

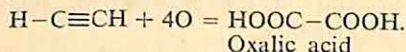


Such a process that involves the union of two or more molecules to form a new (and more complex) molecular aggregate, is known as **polymerisation**. The product is called a *polymer* (*poly* many, *meros* part). Here benzene is a polymer of acetylene. The 'addition' polymer has the same percentage composition as the original compound but obviously a higher molecular weight as nothing is eliminated. The term polymer is applicable to those complex substances that can be directly obtained from simple molecules. Thus, butyric acid, $\text{C}_4\text{H}_8\text{O}_2$, which has a molecular formula exactly twice that of acetaldehyde, $\text{C}_2\text{H}_4\text{O}$, is not a polymer as butyric acid cannot be directly obtained from acetaldehyde. Polymerisation is now better defined as intermolecular combination that is functionally capable of proceeding indefinitely. In condensation type of polymerisation, water or some simple molecule eliminates and the resulting polymer has a composition different from its monomer. Starch, $(\text{C}_6\text{H}_{10}\text{O}_5)_n$, is a condensation polymer of glucose, $\text{C}_6\text{H}_{12}\text{O}_6$.

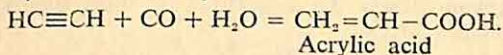
Passed into a strong solution of NH_4Cl and Cu_2Cl_2 at ordinary temperature, acetylene forms vinyl-acetylene, $\text{CH}\equiv\text{C}-\text{CH}=\text{CH}_2$, a colourless gas. On

shaking with aqueous HCl , NH_4Cl and Cu_2Cl_2 at 30° , vinyl-acetylene gives chloroprene, $\text{CH}_2=\text{CCl}-\text{CH}=\text{CH}_2$, a colourless liquid (b.p. 60°). The latter spontaneously forms a linear polymer, called α -polychloroprene, a soft plastic, resembling milled, unvulcanised rubber. This on standing for about 48 hours at 30° , gives **neoprene**, a synthetic rubber which is practically non-inflammable, and resistant to oil.

(10) Chromic acid oxidises acetylene to acetic acid, but alkaline potassium permanganate gives oxalic acid.



(11) Acetylene reacts with carbon monoxide and water in presence of nickel carbonyl to form acrylic acid. It is a commercial process.



(12) Unlike ethylene, acetylene forms a substitution product, dichloroacetylene, C_2Cl_2 , when passed at 0° into sodium hypochlorite solution in absence of light and air.

Uses.—For welding and cutting metals; as an illuminant and an anæsthetic (narcylene). For the manufacture of acetaldehyde, acetic acid and alcohol. As westron, westrosol and hexachloroethane, C_2Cl_6 , a substitute for camphor. For making synthetic rubber (e.g., *Neoprene*) and vinyl plastics and also increasing the growth of pine-apple plants.

Methylacetylene, propene or allylene, $\text{CH}_3\text{C}\equiv\text{CH}$, may be obtained by the action of alcoholic KOH on propylene dibromide, $\text{CH}_3\text{BrCHBrCH}_3$, or acetone dichloride, $\text{CH}_3\text{CCl}_2\text{CH}_3$, some allene, $\text{CH}_2=\text{C}=\text{CH}_2$, is formed in either case. Allylene behaves like acetylene; it adds up water in presence of mercuric salts forming acetone, CH_3COCH_3 , and gives a mercury salt, $(\text{CH}_3\text{C}\equiv\text{C})_2\text{Hg}$, with alkaline $\text{Hg}(\text{CN})_2$. **Butine-2** or crotonylene, $\text{CH}_3\text{C}\equiv\text{CCH}_3$, and **butine-1** or ethylacetylene, $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$, are isomeric and may be prepared in the usual ways; the latter forms a silver or copper derivative but not the former.

Other homologues of acetylene are not important. The members up to $\text{C}_{12}\text{H}_{22}$ are gas or volatile liquid with a characteristic smell. They are soluble in alcohol and other organic solvents and burn with a sooty flame. They resemble acetylene and are prepared likewise. They are isomeric with diolefines.

The acetylenes, C_nH_{n-2} .

Name	Formula	B.P.
Acetylene (Ethine)	$\text{CH}\equiv\text{CH}$	-83°
Methyl acetylene (Allylene)	$\text{CH}_3\text{C}\equiv\text{CH}$	-27°
Ethyl acetylene	$\text{C}_2\text{H}_5\text{C}\equiv\text{CH}$	18°
Propyl acetylene	$\text{C}_3\text{H}_7\text{C}\equiv\text{CH}$	48°
Dimethyl acetylene (Crotonylene)	$\text{CH}_3\text{C}\equiv\text{CCH}_3$	29°
Ethyl methyl acetylene	$\text{CH}_3\text{C}\equiv\text{CC}_2\text{H}_5$	55°

Like diolefines, there are **diacetylenes**, having a pair of triple bonds. Of these, the most notable is dipropargyl, C_6H_6 , an isomer of benzene. Dipropargyl, $\text{HC}\equiv\text{C}-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{CH}$, is a liquid (sp. gr. 0.81) boiling at 85° . It behaves chemically like acetylene, and is prepared from diallyl, $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2$, by bromination and subsequent treatment with alcoholic potash. The monovalent group, $\text{CH}\equiv\text{C}-\text{CH}_2-$, is called **propargyl** (or propinyl).

QUESTIONS

1. Discuss the properties of unsaturated compounds. Give a method for preparing ethylene and name five of its characteristic reactions. (B.Sc. Pass, Dacca Uni. 1939).

2. How would you obtain a current of pure dry ethylene? What is the effect on ethylene of (a) Conc. H_2SO_4 , (b) Chlorine, (c) HClO ? (Inter. B.Sc., England).

3. Write a clear account of the preparation, properties and uses of acetylene. (Inter. B.Sc., England).

4. What do you understand by unsaturation in organic compounds? What reactions are characteristic of this state? (Punjab Inter., 1920).

5. Compare and contrast the chemical properties of paraffins, olefines and acetylenes. Explain clearly the behaviour of these hydrocarbons towards the halogens and halogen acids.

6. Establish the structure of ethylene.

7. How would you prepare several gas jars full of methane, ethylene, and acetylene? What experiments would you make to identify these gases?

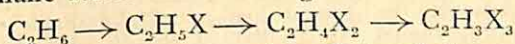
8. What is meant by the term unsaturated compounds? Give a few examples of such substances, showing how their reactions differ from those of saturated compounds. (B.Sc., London, 1933).

9. How do the physical properties of the members of the methane series of hydrocarbons vary with increase in the number of carbon atoms? Describe the preparation of acetylene. What are the characteristic differences in the properties of saturated and unsaturated hydrocarbons? (B.A. & B.Sc. Degree Exam., 1932, Andhra Uni.).

CHAPTER VII

THE HALOGEN DERIVATIVES OF THE PARAFFINS

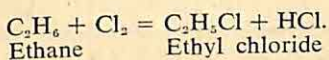
We have seen that the hydrogen atoms of the paraffins are replaced one after another by chlorine or bromine (p. 43) giving halogenated paraffins. Ethane forms the following derivatives:



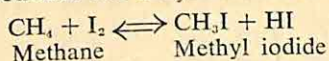
$\rightarrow \text{C}_2\text{H}_2\text{X}_4 \rightarrow \text{C}_2\text{HX}_5 \rightarrow \text{C}_2\text{X}_6$ where X is a halogen atom. They are mono-, di-, tri-, etc., halogen derivatives according to the number of halogen atoms in the molecule. They are highly reactive and may be readily converted into other compounds. Herein lies their importance. Some are used in medicine, e.g., iodoform, CHI_3 , and chloroform, CHCl_3 ; others such as carbon tetrachloride, CCl_4 , are industrial solvents.

Monohalogen derivatives or alkyl halides.—When only one hydrogen atom of a paraffin molecule is replaced by a halogen, we get a mono-halogen derivative, $\text{C}_n\text{H}_{2n+1}\text{X}$.

Preparation.—(1) Alkyl halides may be obtained by the direct action of a halogen upon the paraffins except methane which gives a mixture of all the four substitution products. By controlling the ratio of halogen to paraffin, mono-halides may be obtained. The method is not employed commercially; the mixture is sometimes used as



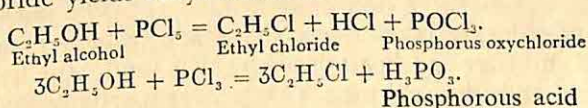
Alkyl iodides cannot be similarly prepared inasmuch as the iodic acid formed reduces the alkyl iodide back to the paraffin:



In presence of iodic acid or mercuric oxide, which decomposes paraffins can, however, be iodinated. Higher paraffins are iodogenated only at high temperature and in presence of catalysts. Alkyl iodides are made by boiling alkyl chlorides or bromides with sodium in methanol or acetone in which NaCl or NaBr is insoluble.



(2) By the action of phosphorus halides on alcohols, corresponding alkyl halides can be conveniently made. Ethyl alcohol with phosphorus penta- or tri-chloride yields ethyl chloride.



PCl_5 or PCl_3 replaces the hydroxyl group, $-\text{OH}$, by chlorine. We shall come across many similar cases later on. To prepare alkyl bromides and iodides, the phosphorus halide is prepared *in situ* by treating a mixture of red phosphorus and bromine or iodine with the alcohol.

Preparation of ethyl bromide.—75 c.c. of ethyl alcohol (dried over quicklime) and 15 g. of red phosphorus are taken in a distilling flask fitted with a tap-funnel and joined to a Liebig's condenser and a receiver. The receiver is connected to a soda-lime tower which absorbs the fumes of hydrobromic acid formed. 20 c.c. of bromine are taken in the tap-funnel. The flask is placed in a cold water-bath and the bromine added drop by drop. The reaction starts immediately with evolution of heat. When all the bromine has been added, the flask is allowed to stand for some hours. The contents are then distilled over by replacing the tap-funnel by a thermometer and using a long (or coil) condenser. The distillate up to 60° is collected, which contains ethyl bromide (b.p. 38.5°), alcohol, hydrobromic acid, etc. The receiver is kept cool with iced-water to prevent loss of ethyl bromide which is very volatile. In a separating funnel, the distillate is shaken with sodium carbonate solution to remove hydrobromic acid, alcohol dissolves in the water. Ethyl bromide, being insoluble in water, separates at the bottom. It is dried with fused calcium chloride and re-distilled.

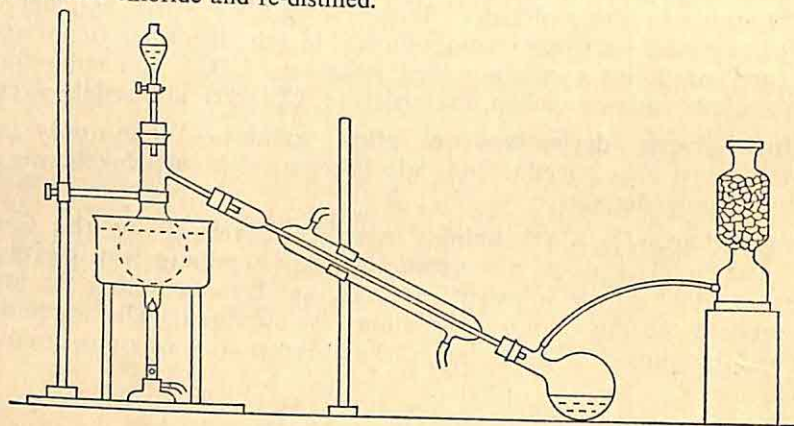
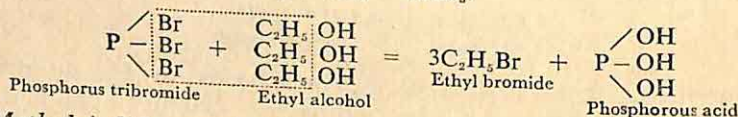
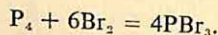
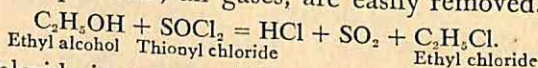


Fig. 25. Preparation of ethyl bromide.



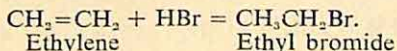
Methyl iodide or *ethyl iodide* may be prepared likewise by adding the requisite quantity of iodine, a little at a time, to a mixture of alcohol and red phosphorus, followed by distillation from water-bath after several hours. The alkyl chlorides are better prepared with thionyl chloride, $SOCl_2$. Thionyl bromide is very unstable; thionyl iodide does not exist. The co-products, all gases, are easily removed.



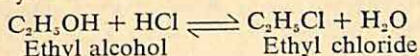
Methyl chloride is commercially made from the waste products of beet-sugar industry by heating with HCl , and also by passing cheap natural gas and dry chlorine (10:1) over partially reduced $CuCl_2$ at 450° (traces of other chloroderivatives of methane are formed). Method (4) is, however, more important. It is a fire extinguisher, refrigerant, a local anæsthetic and a methylating agent in the dyestuff industry.

(3) Alkyl halides are also formed when halogen acids act on the

olefines (p. 58). The addition takes place rather slowly, and generally follows Markownikoff's rule.



(4) Alkyl halides are conveniently prepared by the action of halogen hydracids on alcohols in presence of a dehydrating agent such as zinc chloride or H_2SO_4 . The latter removes the water formed and prevents the opposite reaction. Commercially, methanol and HCl gas are passed over alumina gel or activated carbon at about 350° to get methyl chloride, and 95% ethanol and HCl gas under 30 lb. pressure into 45% ZnCl_2 solution at 145° to obtain ethyl chloride. Alkyl halides are, therefore, regarded as alkyl salts or *esters*.

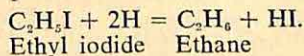


Preparation of ethyl chloride.—Absolute ethyl alcohol and half its weight of anhydrous zinc chloride are taken in a flask fitted with an upright condenser and a side-tube. Hydrochloric acid gas (generated by dropping strong H_2SO_4 on strong HCl) is passed into the alcohol through the side-tube until saturated. The flask is then gently warmed on water-bath. The top of the condenser is connected to a series of washers containing water, dilute caustic potash and strong sulphuric acid successively. These remove alcohol, hydrochloric acid and moisture respectively which accompany ethyl chloride. The gas is finally condensed to a liquid (b.p. 12.5°) in a U-tube connected to the last washer, and kept immersed in a freezing mixture. Other alkyl chlorides may be similarly prepared by taking the corresponding absolute alcohol. The halogen acid may be replaced by concentrated sulphuric acid and sodium halide.

Ethyl chloride is used for producing local insensibility in minor surgical operations and for making tetraethyl lead, an antiknock, and ethyl cellulose, a plastic. Methyl and ethyl chloride are refrigerating agents. Methyl bromide extinguishes fire by forming a blanket of heavy gas which cuts off oxygen; it is used chiefly in aircrafts as a fire extinguisher and for killing weevil in flour by fumigation.

Properties of alkyl halides.—The lower members are colourless, oily liquid with characteristic smell, and immiscible with water. They are readily soluble in alcohol or ether and usually heavier than water. Methyl chloride, methyl bromide and ethyl chloride are colourless gases at ordinary temperature. Alkyl bromides and iodides darken gradually if exposed to light due to slight decomposition. They may be decolorised by shaking with a little mercury or finely divided silver. Some of them burn with a smoky flame. Alkyl halides are quite reactive—the halogen atom can be readily replaced by other atoms or radicals; iodine is most easily removed, then bromine and then chlorine. This is because the $\text{C}-\text{X}$ bond strength increases in the following order $\text{C}-\text{I}$, $\text{C}-\text{Br}$, $\text{C}-\text{Cl}$. Methyl halides are more reactive than the corresponding ethyl halides. The reactions of ethyl iodide may be taken as typical.

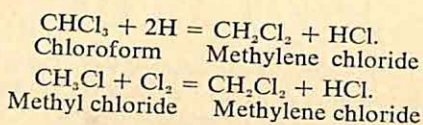
Reactions of ethyl iodide, $\text{C}_2\text{H}_5\text{I}$.—(1) It gives ethane on reduction with nascent hydrogen (from zinc and hydrochloric acid, or aluminium-mercury couple and methyl alcohol).



$\text{CH}_3-\text{CHX}-\text{CH}_3$. The former, normal propyl halide, has its halogen attached to a primary carbon atom, while the latter, isopropyl halide, to a secondary.

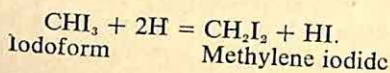
Dihalogen derivatives of the paraffins.—When two hydrogen atoms in a paraffin are replaced by halogen, we get a dihalogen derivative or alkylene halide, $\text{C}_n\text{H}_{2n}\text{X}_2$. The halogen may be attached to the same or different carbon atoms. Dichloroethane, $\text{C}_2\text{H}_4\text{Cl}_2$, is either $\text{CH}_2\text{ClCH}_2\text{Cl}$ or CH_3CHCl_2 . The dihalogen derivatives may be directly obtained by the action of halogen on paraffins or olefines, or of halogen acids on acetylenes (p. 67). The simplest is methylene chloride.

Methylene chloride, CH_2Cl_2 , is prepared by reducing chloroform in alcohol with zinc dust and hydrochloric acid. It is formed when methyl chloride is chlorinated.



Commercially, it is obtained as a by-product in the manufacture of chloroform from carbon tetrachloride (p. 78). Methylene chloride is a colourless, heavy liquid (sp. gr. 1.337) boiling at 42° . It is used as a refrigerant, dewaxing agent in petroleum refining, paint and varnish remover, and for extracting caffeine from tea and coffee.

Methylene iodide, CH_2I_2 , or di-iodomethane is prepared by reducing iodoform with alkaline arsenite solution, or with hydriodic acid and phosphorus. The yield in the former case is almost quantitative.



Methylene iodide is a colourless, very heavy liquid (sp. gr. 3.29) boiling at 180° . It is used in organic synthesis and separating heavy minerals from substances of sp. gr. less than 3.0. Mixtures of methylene iodide and benzene give liquids of any density between 0.8 and 3.29 and are useful for gravity separation. Halogens in methylene halide are less reactive than those in the corresponding methyl halides.

Methylene iodide can apparently be represented in two ways:

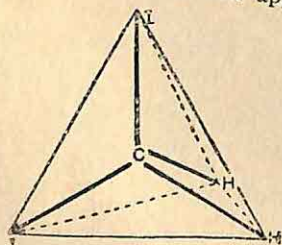
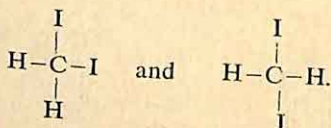


Fig. 26. Methylene iodide.

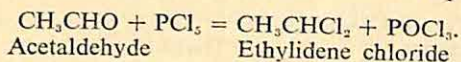


But only one is known. This is explained by assuming that the valencies of carbon are directed in space towards the four apexes of a regular tetrahedron (p. 60). Evidently only one such arrangement is possible (Fig. 26).

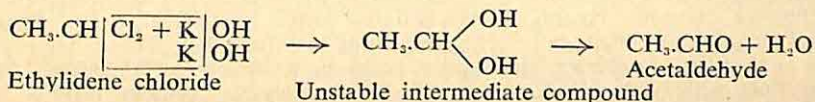
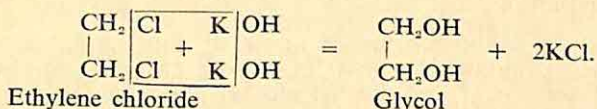
Dichloroethane, $\text{C}_2\text{H}_4\text{Cl}_2$, is either ethylene chloride, $\text{ClH}_2\text{C}-\text{CH}_2\text{Cl}$,

or ethylidene chloride, $\text{CH}_3-\text{CHCl}_2$. Ethylene chloride is commercially prepared by the action of chlorine on ethylene (p. 58). It is a liquid (b.p. 84°); it is a solvent for fats and a fumigant. *Thiokol*, a synthetic rubber, is made from ethylene chloride and sodium polysulphide.

Ethylidene chloride is prepared by the action of phosphorus pentachloride on acetaldehyde. It is a colourless liquid boiling at 60° .



Ethylene and ethylidene chloride behave differently. Boiling aqueous caustic potash replaces the halogen by a hydroxyl group in both cases. One yields glycol, and the other acetaldehyde. This shows that ethylidene chloride has both the halogens attached to the *same* carbon.

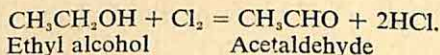


Ethylene dibromide, $\text{CH}_2\text{Br}.\text{CH}_2\text{Br}$, a liquid boiling at 132° , is used with tetraethyl lead (an anti-knock compound in automobiles) for eliminating lead (which causes pitting) as PbBr_2 from the cylinder.

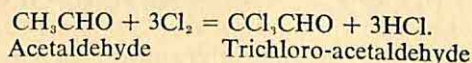
Trihalogen derivatives of the paraffins.—Of these only two are important, viz., chloroform and iodoform, for their use in surgery and medicine respectively.

Chloroform, CHCl_3 .—(1) In the laboratory or commercially, chloroform is prepared by distilling a mixture of aqueous ethyl alcohol or acetone and bleaching powder. The latter supplies chlorine and lime necessary for chlorination and hydrolysis.

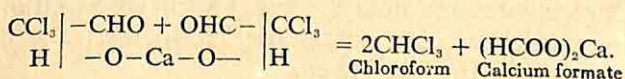
(i) Alcohol is first oxidised by chlorine to acetaldehyde:



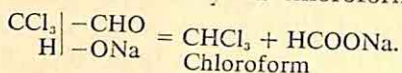
(ii) Acetaldehyde is then chlorinated to trichloro-acetaldehyde or chloral:



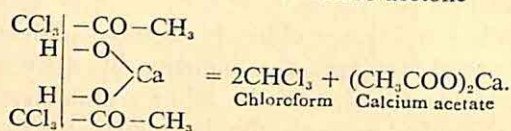
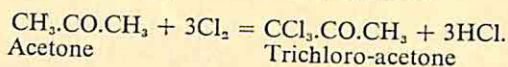
(iii) Finally, chloral is hydrolysed by lime to chloroform and calcium formate:



Chloral and caustic soda also yield chloroform:



Chloroform made from acetone contains mono- and di-chloro-acetone which are poisonous. It is unsuitable for medicinal purposes. Surgical chloroform is usually made from chloral.



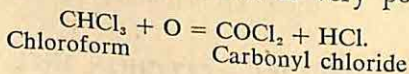
All compounds with a $\text{CH}_3\text{CO}\cdot$ or $\text{CH}_3\text{CH}(\text{OH})$ group yield chloroform with chlorine and alkali.

Preparation.—In a round-bottomed litre-flask, fitted with a delivery tube and a condenser, is introduced a paste made with 150 g. of bleaching powder and 500 c.c. of water. 35 c.c. of ethyl alcohol are thoroughly mixed with it by shaking. The flask is slowly heated on a sand-bath. At the beginning the reaction is vigorous, heating is discontinued until it slackens. The flask is again heated, and distillation continued until no more oily drops pass over. The end of the condenser dips under water in a beaker. Chloroform being immiscible with, and heavier than, water, occupies the bottom layer. It is removed with a separating funnel, washed several times with dilute caustic soda and water, and dried with fused calcium chloride. It is next re-distilled on water-bath. For pure chloroform, chloral is treated with caustic soda likewise.

(2) A modern method involves the partial reduction of carbon tetrachloride, CCl_4 , with steam and iron powder, $\text{CCl}_4 + 2\text{H} = \text{CHCl}_3 + \text{HCl}$. Carbon tetrachloride, being cheap, is the principal source of CHCl_3 in U.S.A. Methylene chloride is a bye-product.

(3) When an electric current is passed into 20% NaCl containing acetone, chloroform is evolved. It is a commercial process in U.S.A.

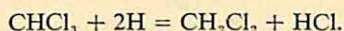
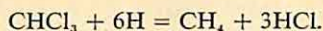
Properties.—Chloroform is a heavy (sp. gr. 1.5), colourless, non-inflammable liquid (b.p. $61\text{--}62^\circ$) with a characteristic pleasant smell. It is practically insoluble in water but readily soluble in alcohol or ether. It is an anæsthetic; Simpson first used it in 1848 in Edinburgh, and saved patients from the horror of surgical operation. Exposed to light and air, chloroform decomposes into chlorine, hydrochloric acid, carbonyl chloride, COCl_2 , etc.; the last is very poisonous.



To arrest this decomposition, chloroform is stored in bottles of amber colour, full to the neck, with about 1% of absolute alcohol which is believed to combine with COCl_2 to form innocuous ethyl carbonate, $(\text{C}_2\text{H}_5\text{O})_2\text{CO}$. Pure chloroform does not react with silver nitrate solution, but the decomposed sample, containing HCl , yields a white ppt. Purity of chloroform may thus be tested.

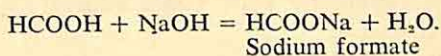
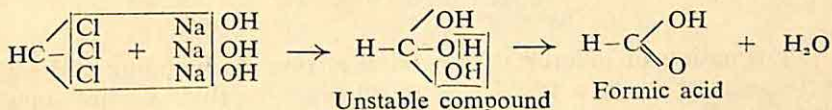
Chloroform produces greater muscular relaxation than any other anæsthetic but tends to inhibit the action of the heart. So it is employed mixed with other inhalant drugs such as ether. Chloroform has been largely replaced by other anæsthetics.

Chloroform is reduced to methane by zinc dust and water at high temperature, and to methylene chloride by zinc and hydrochloric acid (p. 76).

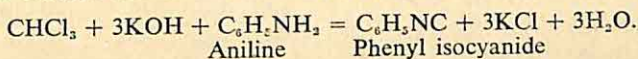


Methylene chloride

On heating with alcoholic caustic soda, it decomposes as



1-2 drops of chloroform is warmed with a little aniline and alcoholic potash; disgusting odour of phenyl isocyanide or carbylamine is perceptible. It is a very delicate test for chloroform as also for aniline.

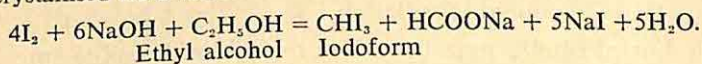


Uses.—Chloroform is an anæsthetic and an industrial solvent, particularly for alkaloids, resins and oils; it is a preservative for decoctions. It is used in dry cleaning. Spirit chloroform is a hypnotic and a sedative in medicine.

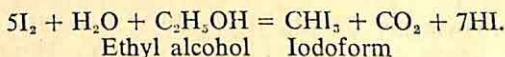
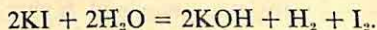
Bromoform, CHBr_3 , a liquid (b.p. 148°), is made in the same way as chloroform. It has a high sp. gr. (2.88) and so is used in mineral analysis by floatation method. It was in the past used as a sedative in whooping cough, sea sickness and asthma.

Iodoform, CHI_3 , is prepared by the action of iodine and alkali on ethyl alcohol or acetone. The mechanism of the reaction is similar to that of chloroform.

Preparation.—30 g. of sodium carbonate is dissolved in 100 c.c. of hot water in a beaker and kept at 70° . To this, are added slowly with stirring, 20 c.c. of alcohol and 10 g. of iodine. The mixture turns pale yellow and on cooling yellow crystals of iodoform separate. These are filtered, washed with cold water, and re-crystallised from alcohol. Caustic soda may replace sodium carbonate.

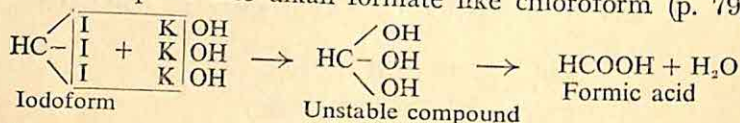


Iodoform is manufactured by the electrolysis of a dilute ethyl alcoholic or acetone solution of potassium iodide in presence of sodium carbonate:

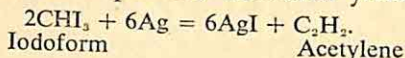


Properties.—Iodoform is a pale yellow, crystalline solid (m.p. 119°)

with a strong, sickly smell. It is insoluble in water but soluble in warm alcohol. It is an antiseptic in surgery generally in the form of an iodoform gauze. Iodoform sublimes readily. It resembles chloroform in its chemical behaviour. On heating with caustic alkali, iodoform decomposes into alkali formate like chloroform (p. 79).



When heated with silver powder, iodoform yields acetylene:

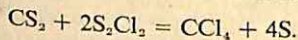
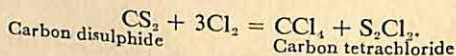


Formation of iodoform from ethyl alcohol with iodine and sodium carbonate serves as a test for ethyl alcohol (methyl alcohol does not give it). But any compound with $\text{CH}_3\text{--CO--C}$, or $\text{CH}_3\text{--CHOH--}$ group responds to this test.

Fluoroform, CHF_3 , obtained from bromoform or iodoform and mercuric fluoride, is a very stable gas, practically non-toxic.

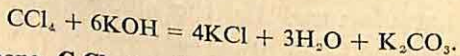
Carbon tetrachloride, CCl_4 .—When all the hydrogen atoms of a paraffin are replaced by halogen, we get a halide of carbon. Several such halides are known, e.g., CCl_4 , CBr_4 , C_2Cl_6 , etc. Of these, carbon tetrachloride is the most important for its extensive use as a solvent for rubber, fat and grease. It is a toxic, non-inflammable, colourless, and heavy liquid, stable at red heat. It is soluble in alcohol or ether. Carbon tetrachloride (b.p. 76°) is used as a fire extinguisher under the trade name *pyrene*, and also in dry cleaning. It kills hookworm, the average dose for adults being 2.5 c.c. Freon is made from carbon tetrachloride.

It is manufactured from carbon disulphide and chlorine at $40^\circ\text{--}60^\circ$ in presence of manganese chloride or iron powder. Sulphur chloride chlorinates fresh CS_2 to CCl_4 ; the sulphur is reconverted into carbon disulphide.



U.S.A. makes it by chlorinating methane from natural gas at $250^\circ\text{--}400^\circ$. The reaction is exothermic and HCl is a bye-product. CCl_4 is separated by fractional distillation.

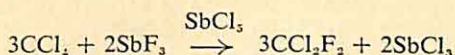
With hot alcoholic potash, carbon tetrachloride splits into K_2CO_3 , KCl and H_2O .



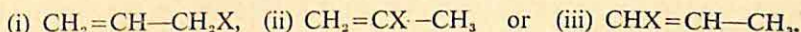
Hexachloro-ethane, C_2Cl_6 , a volatile solid (m.p. 185°) smelling like camphor, is a contact insecticide, non-toxic to man and higher animals. It is used for killing mosquito larvae.

Diffuorodichloromethane, CF_2Cl_2 , (b.p. -30°) is widely used as a refrigerant in air conditioning under the trade name Freon. The gas liquefies easily under pressure and the heat of vaporisation of the liquid is quite large. It is made from carbon tetrachloride and antimony trifluoride using antimony penta-

chloride as a catalyst. It is very stable, non-corrosive and practically odourless, and so, better than ammonia, sulphur dioxide or ethyl chloride. It is neither toxic nor inflammable.

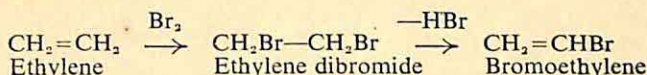


Besides these, there are halogen derivatives of unsaturated hydrocarbons. In these, the halogen may be attached to the carbon atom having a double bond, or to one which is singly linked e.g.,

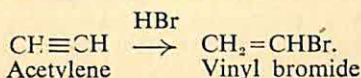


Their properties as well as mode of preparation are different. The first type, however, behaves like alkyl halides. Bromo-ethylene, $\text{CH}_2=\text{CHBr}$, and allyl iodide, $\text{CH}_2=\text{CH}-\text{CH}_2\text{I}$, of this group are largely used in various syntheses.

Vinyl bromide or **bromo-ethylene**, $\text{CH}_2=\text{CHBr}$, is usually prepared from ethylene by bromination and subsequent treatment with alcoholic potash when hydrobromic acid is removed:

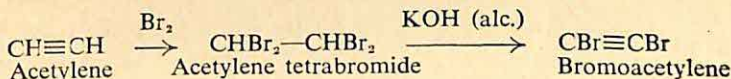


Acetylene gives vinyl bromide with HBr (p. 67) :



Vinyl chloride, $\text{CH}_2=\text{CHCl}$, made from acetylene and HCl, is a colourless gas that readily polymerises under the effect of heat and catalyst to polyvinyl chloride (PVC). It is a white plastic widely used in making curtains, rain coats, bags, etc.

Other halogeno-unsaturated hydrocarbons may be similarly prepared :

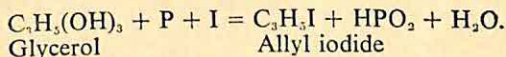


Calcium carbide, when treated with iodine at very low temperature in potassium iodide solution, yields C_2I_4 and C_2I_2 . Passed into a solution of iodine in liquid ammonia, acetylene forms C_2I_2 .



Tetrafluoroethylene, C_2F_4 , a colourless gas, made from chloroform and SbF_3 at 650° , polymerises readily to a white plastic (Teflon & Fluon) which is extremely inert chemically (it is unaffected by boiling *aqua regia*) and a very good electric insulator.

Allyl iodide, a liquid boiling at 103° , is prepared from glycerol with phosphorus and iodine. The reactants should be present in right proportion, otherwise isopropyl iodide, $\text{CH}_3\text{CHICH}_3$, is formed.



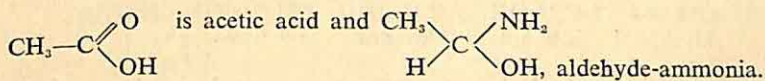
QUESTIONS

1. Describe the preparation of chloroform. What are its chief uses? What products are formed when chloroform is exposed to the action of (i) air and sunlight, (ii) KOH solution? (Pre. Med., England).
 2. State what compounds are capable of yielding CHCl_3 on treatment with bleaching powder. Explain the course of the reactions, and describe how you would prepare pure specimens of chloral alcoholate, chloral, and iodoform. (B.Sc., London, 1933).
 3. A liquid may be chloroform, carbon tetrachloride or acetylene tetrachloride. By what reactions can it be identified?
 4. List the typical reactions of the alkyl halides with equations, and point out their significance.
 5. Give an account of the general methods of preparation of halogen substitution products of the paraffins.
 6. Discuss the action of KOH, AgCN, ammonia and sodium upon propyl iodide. Give equations.
 7. How would you test for chloroform in presence of iodoform? (B.Sc., Punjab, 1933).
 8. Describe the preparation of iodoform. (B.Sc., Punjab, 1931).
 9. Describe the preparation of chloroform, giving a neat sketch of apparatus used. How is this substance identified, and what is the action of caustic potash solution on it? (B.Sc. Pass, Dacca Uni., 1934).
 10. Describe, with a careful sketch, the preparation of a specimen of pure chloroform from alcohol, and explain the reactions which occur. What is chloroform used for? What are its chief properties and reactions? (B.Sc. pass, Calcutta Uni. 1940).
 11. How would you prepare a specimen of chloroform in the laboratory? State its properties and uses. How would you test its presence in a liquid? (B.A. Degree Exam., 1942, Madras Uni.).
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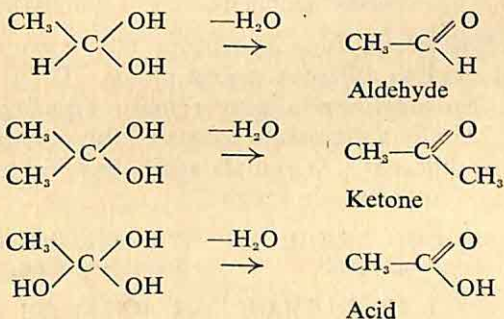
CHAPTER VIII

THE ALCOHOLS

When one or more hydrogen atoms of the paraffins are replaced by a corresponding number of hydroxyl (-OH) groups, we get a series of compounds known as **alcohols**. They are, therefore, hydroxy-paraffins. Alcohols having one hydroxyl group are monohydric, those with more are generally called polyhydric alcohols. Thus, methyl alcohol, CH_3OH , is a monohydric, ethylene glycol, $\text{HOH}_2\text{C}-\text{CH}_2\text{OH}$, a dihydric and glycerol, $\text{HOH}_2\text{C}.\text{CH}(\text{OH}).\text{CH}_2\text{OH}$, a trihydric alcohol, the latter two coming under polyhydric alcohols. Any hydroxy-compound, however, is not an alcohol, *e.g.*,



Two or more hydroxyl groups are seldom attached to the *same* carbon atom. In such cases, water eliminates and various compounds result:



Alcohols are further divided into **primary**, **secondary** and **tertiary**.

(a) Primary alcohols contain $-\text{CH}_2\text{OH}$ group *i.e.*, the carbon bearing the hydroxyl group is linked to at least *two* hydrogen atoms. The monovalent $-\text{CH}_2\text{OH}$ group is at either end of a straight chain, *e.g.*, ethyl alcohol, $\text{CH}_3.\text{CH}_2\text{OH}$.

(b) Secondary alcohols have the hydroxyl group attached to a carbon to which only *one* atom of hydrogen is linked, *i.e.*, the $-\text{CHOH}-$ group is present in these; *e.g.*, isopropyl alcohol, $\text{CH}_3.\text{CHOH}.\text{CH}_3$. The divalent $-\text{CHOH}-$ group may be in any position except the ends in a straight chain.

(c) In tertiary alcohols, the hydroxyl group is linked to a carbon having *no* hydrogen *i.e.* the $>\text{C}(\text{OH})-$ group occurs in them; tertiary butyl alcohol, $(\text{CH}_3)_3\text{COH}$, is an example.

Nomenclature and isomerism of the alcohols.—There are three ways of naming alcohols. The oldest is to name after the group to which the hydroxyl group is attached, *e.g.*,

$\text{CH}_3\text{—OH}$,
Methyl alcohol

$\text{CH}_3\text{CH}_2\text{—OH}$,
Ethyl alcohol

$(\text{CH}_3)_2\text{CHCH}_2\text{—OH}$.
Iso-butyl alcohol, etc.

Here the surname, alkyl group, precedes the family name alcohol. This is not satisfactory for naming a fairly large number of isomeric alcohols derived from pentane (giving 8), hexane (17), heptane (38), etc. In the second manner, 'e' at the end of a paraffin is changed into 'ol.' The Geneva system is applied, the side-chain is numbered and also the —OH group located by a number.

CH_4 Methane	C_2H_6 Ethane	C_6H_{14} Hexane	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{—CH}_2\text{—CH—CH}_2\text{OH} \end{array}$ 2-methyl-1-butanol
CH_3OH Methanol	$\text{C}_2\text{H}_5\text{OH}$ Ethanol	$\text{C}_6\text{H}_{13}\text{OH}$ Hexanol	$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2(\text{OH})$ 1,2-propanediol

In the third, alcohols are expressed as derivatives of methyl alcohol, the simplest member, which is called *carbinol* (*carbine alcohol*).

$\text{CH}_3\text{—OH}$
Carbinol

$(\text{CH}_3)_2\text{CH—OH}$
Dimethyl carbinol

$\text{CH}_3\text{—CH}_2\text{—C}(\text{CH}_3)_2\text{H—OH}$
Ethylmethyl carbinol

The hydroxyl group may substitute any hydrogen in a carbon chain, and be linked to different carbon atoms. We thus have isomeric alcohols. The hydroxyl group may remain attached to a particular carbon in the chain, but the arrangement of the remaining hydrocarbon portion may be different. We shall again have isomers. Thus butyl alcohol exists in four isomeric forms:

$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{OH}$,
Primary *n*-butyl alcohol

$\text{CH}_3\text{—CH}_2\text{—CHOH—CH}_3$,
Secondary *n*-butyl alcohol

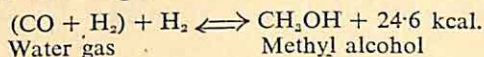
$(\text{CH}_3)_2\text{CH—CH}_2\text{OH}$ and $(\text{CH}_3)_3\text{C—OH}$
Primary isobutyl alcohol Tertiary butyl alcohol

The monohydric alcohols have the general formula $\text{C}_n\text{H}_{2n+1}\text{OH}$, and may be looked upon as alkyl hydroxides, R—OH . They apparently resemble metallic hydroxides. If the alkyl group is unsaturated, we have an unsaturated alcohol. The most important are methyl alcohol, CH_3OH , and ethyl alcohol, $\text{CH}_3\text{CH}_2\text{OH}$.

Methyl alcohol, CH_3OH , methanol. wood-naphtha or wood-spirit (Greek *methu*, wine; *hule*, wood) occurs in combined state in pectin and some essential oils, *e.g.*, oil of wintergreen which is methyl salicylate. By general methods of preparation (*q.v.*) one may but never does, obtain methyl alcohol. It is manufactured by the following methods:

Synthetic process.—Most of the methanol of commerce is made by passing purified water gas with half its volume of hydrogen under

pressure (200-300 atmospheres) over a mixture of oxides of zinc and chromium or a chromate, heated to 350°-400°. In U.S.A. the mixture, $\text{CO} + 2\text{H}_2$, is obtained by the partial oxidation of methane (of natural gas) with oxygen from liquid air.



The conversion is 20-25% depending upon conditions. A little of other alcohols *e.g.*, butanol, is also formed together with some methane, CO_2 , etc. Since water gas is made by passing steam over red-hot coke ($\text{C} + \text{H}_2\text{O} = \text{CO} + \text{H}_2$), this may be regarded as a 'synthesis from elements.'

Another commercial synthesis consists of heating CO_2 and H_2 under pressure in presence of ZnO ; other products *e.g.*, methane are also formed.



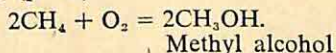
In 1955, U.S.A. produced 204 million gallons of synthetic methanol and only 2.3 of wood-spirit, the former more cheaply. The world production of synthetic methanol is about $2\frac{1}{2}$ lac tons, that of wood-spirit only 25 thousand tons. Methanol (in U.S.A.) was a dollar a gallon in 1919 but only 30 cents in 1955.

From wood.—When wood (with 15-20% moisture) is heated in large iron retorts, out of contact with air (destructive distillation), for about 30 hours to 350°-400°, we obtain:

- (i) an inflammable mixture of gases ('wood gas') consisting mainly of methane, carbon monoxide, carbon dioxide and nitrogen (25%).
- (ii) an aqueous distillate called 'pyroligneous acid' (*pyro*, fire; *lignum*, wood), containing methyl alcohol (2-4%), acetone (up to 0.5%), acetic acid (about 8%), and traces of other substances (45%).
- (iii) wood-tar having phenolic bodies and other substances (5%), and
- (iv) wood charcoal, left in the retort (25%).

Roughly, wood yields about 1% of its weight of methanol. It comes from lignin which has methoxy ($\text{CH}_3\text{O}-$) groups. The wood gas heats the wood for distillation. Pyroligneous acid with the tar distils over. On standing, a reddish brown, aqueous liquid separates. It is removed and distilled from a copper vessel. The vapour is led through hot milk of lime to get calcium acetate. Methyl alcohol (b.p. 64.5°), acetone (b.p. 56°) and water pass over and are condensed. By fractional distillation over quicklime, methyl alcohol is separated. The residue of fermented beet-root molasses is likewise distilled for methyl alcohol.

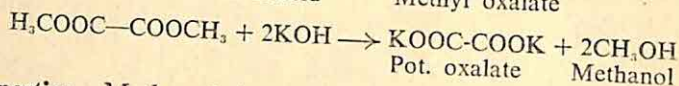
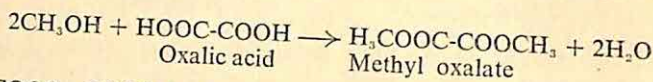
Methyl alcohol is also made by incomplete combustion of methane, *e.g.*, by passing CH_4 and O_2 under 100 atmospheres through a copper tube at 200°; the conversion is about 17% (p. 43).



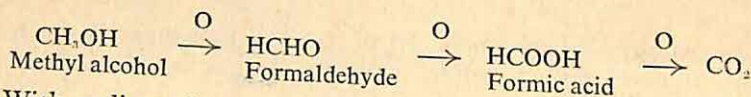
The only wood distillation factory at Bhadrawati makes about 420 tons of methyl alcohol per year.

Purification.—Commercial wood-spirit contains 1-2% of acetone (detected by the iodoform test, p. 79) which is removed by dry chlorination of the hot liquid followed by fractional distillation. Trichloro-acetone remains behind and

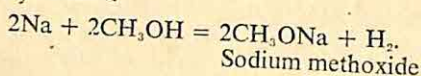
pure methanol passes over. By treating wood-spirit with fused calcium chloride, a crystalline compound, $\text{CaCl}_2 + 4\text{CH}_3\text{OH}$, is obtained. This is separated and the residual acetone squeezed out; methanol is recovered by distillation. Pure methanol may be obtained by treating with oxalic acid; solid methyl oxalate formed is washed with water to remove acetone and then boiled with caustic potash; methanol and water distil over. It is dried over freshly ignited quicklime and redistilled.



Properties.—Methanol is a colourless liquid (b.p. 64.5°) with a pleasant odour and a burning taste. It is poisonous, causing blindness, madness and death depending upon the dose. In the body it is slowly oxidised to formic acid (which is toxic) and not to innocuous CO_2 . It is, therefore, used to 'denature' *i.e.*, render unfit for drinking ethyl alcohol (for making methylated spirit). Methanol is miscible in all proportions with, and lighter than, water. On oxidation, it finally gives carbon dioxide:



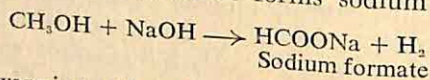
With sodium, it reacts vigorously and gives sodium methoxide, a solid. Methanol is a very weak acid ($K_A = 1 \times 10^{-17}$); methoxides are readily hydrolysed by water.



Magnesium methoxide, made likewise, is used to remove the last traces of water from methanol: $\text{Mg}(\text{OCH}_3)_2 + \text{H}_2\text{O} = 2\text{CH}_3\text{OH} + \text{MgO}$.

With conc. H_2SO_4 , it first gives methyl hydrogen sulphate, CH_3HSO_4 , and finally dimethyl sulphate, $(\text{CH}_3)_2\text{SO}_4$.

Heated with soda-lime, methanol forms sodium formate:

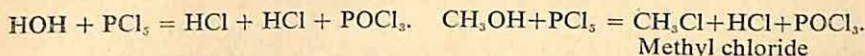
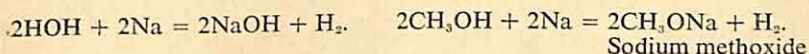


Tests: (i) On warming with a few drops of conc. H_2SO_4 and a pinch of salicylic acid, methyl salicylate with a characteristic odour is formed.

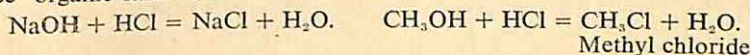
(ii) A red-hot piece of copper gauze is dropped into a test-tube containing a few drops of methyl alcohol. The alcohol is oxidised to formaldehyde having a pungent odour, and the copper gauze becomes bright due to reduction. Methyl alcohol does not give iodoform reaction like ethyl alcohol.

Uses.—Methyl alcohol is chiefly employed for making formaldehyde, dyestuffs, perfumes, pharmaceuticals, varnishes, polishes, etc. and also as a solvent for castor oil, ethyl cellulose, colophony. Mixed with methyl acetate and acetone, methyl alcohol forms an excellent solvent for lacquer. It is used as an antifreeze for the automobile in U.S.A. and also for making methylated spirit. In Germany, it is one of the constituents of an alcohol-petrol fuel.

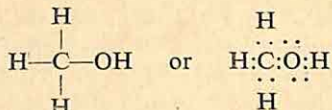
Structure of methyl alcohol.—Methyl and other alcohols behave like hydroxides towards metallic sodium, phosphorus pentachloride, etc.



Acids react with caustic soda producing salt and water; with alcohols, they produce 'organic salts' or *esters* and water:



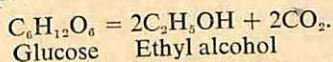
Like water of crystallisation, methanol enters into some crystalline salts, e.g., $\text{CaCl}_2 \cdot 4\text{CH}_3\text{OH}$ or $\text{MgCl}_2 \cdot 6\text{CH}_3\text{OH}$. Alcohols are alkyl derivatives of water, i.e., ROH . From analytical data, methyl alcohol is CH_4O . Of the four hydrogen atoms, only one is replaceable by sodium. PCl_5 removes an $-\text{OH}$ group and the product, CH_3Cl , has no replaceable hydrogen. Methyl alcohol is formed when methyl chloride, CH_3Cl , reacts with aqueous caustic potash: $\text{CH}_3\text{Cl} + \text{KOH} = \text{CH}_3\text{OH} + \text{KCl}$, which indicates an $-\text{OH}$ group. With normal valencies of C, O and H, the only way of representing methyl alcohol is



In alcohols, R-OH , the electron-repelling alkyl group makes electrons on the oxygen atom more readily available; the hydrogen atom, therefore, ionises less readily than in water. Alcohols have consequently a lesser tendency to form hydrogen bonds by which they associate. CH_3OH with a higher mol. wt. boils at a much lower temperature than water, due to a lesser tendency to associate. The analogy between alkyl hydroxides and inorganic hydroxides is only superficial, the former being neutral.

Ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$.—By far the most important is ethyl alcohol, the next homologue, simply called *alcohol*. It is known in commerce as 'spirit of wine' or grain alcohol and is manufactured by the fermentation of sugar solutions with yeast, from ethylene (p. 59) or acetylene (p. 68). In 1955 U.S.A. made 80% of her industrial alcohol by synthetic process.

Yeast is a low form of plant life, consisting of only one cell with a thin coating of cellulose around it. Unlike green plants, yeast does not derive its principal food from outside air and water but lives upon decaying animal and vegetable matters, the energy necessary for its growth coming from the decomposition of sugar-like bodies. Thus, if a few yeast cells be added to a *dilute* aqueous solution of glucose (grape-sugar) kept at $20^\circ\text{--}30^\circ$, the liquid begins to froth shortly. Carbon dioxide evolves, which makes it appear boiling, though there is scarcely any rise of temperature. About 95% of the sugar is thus converted into ethyl alcohol and carbon dioxide through some intermediate steps:



A. Lavoisier (1789) expressed this reaction quantitatively as

Grape juice = alcohol + carbon dioxide, the first chemical equation.

Such chemical change brought about by 'living cells' is known as fermentation (*fervere*, to boil). Complex organic molecules are thus broken into much simpler ones. Fermentation has been used from the earliest times for making alcoholic beverages. The reaction is catalytic, the bio-catalyst here is a highly complex organic substance known as enzyme (from Greek, *en* and *zyme*, meaning 'leaven') secreted

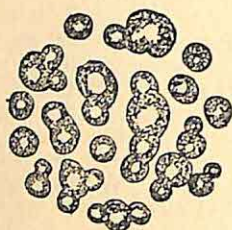
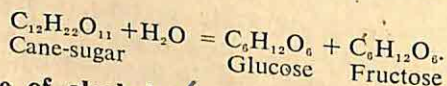


Fig. 27. Yeast cells (Highly magnified).

by plants and animals. To obtain purified protein, E. Buchner (1897) ground yeast with sand, filtered off broken cells and added sugar solution as a preservative to the filtrate. Strangely enough, the cell-free extract fermented the sugar rapidly. The enzyme, *zymase*, can be obtained from the dry, powdered yeast cell by pressure or with solvents. Fermentation is not directly a vital process as formerly believed. *Zymase* owes its origin to living matter, no doubt, but is itself devoid of life. During fermentation, there is liberation of energy which sustains the

yeast plant. Yeast cells, added to a sugar solution, grow and divide, and thus multiply themselves rapidly. Pasteur (1822-1895) obtained one kilogram of yeast from one pin's head size of yeast cells. Enzymes, which are proteins, bring about most of the metabolic changes in plants and animals; they are soluble in water or dilute alcohol and precipitated by neutral salts. They are usually active between 20°-55° and pH 2-8, and susceptible to small changes of temperature and pH. Most of them become inactive on heating their solution above 80° for a while. Enzymes are mostly hydrolytic but some are oxidising-reducing also. Most enzymes derive their names from the substances they act upon, by adding *-ase*, e.g., *maltase* splits up maltose. The action of an enzyme is selective—it cannot decompose any substance, just as one key cannot open every lock. Thus, *zymase* cannot produce alcohol from cane-sugar. Besides *zymase*, yeast generally contains another enzyme *sucrase* or *invertase* which hydrolyses cane-sugar into isomeric glucose and fructose (or invert sugar). These are then decomposed by *zymase* into alcohol and carbon dioxide. That is why when yeast is added to cane-sugar solution, the fermentation action becomes visible only after some time.

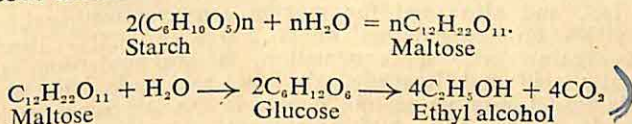


Manufacture of alcohol. (Alcohol is made from cheap materials such as potato, maize, oat, rice, etc., and also waste molasses from sugar factories, but never from costly cane-sugar.) Cereals like rice, maize, etc., or potatoes consist mainly of starch, ($\text{C}_6\text{H}_{10}\text{O}_5$)_n, a high polymer of glucose. Starch is hydrolysed to glucose which, with yeast, yields alcohol. (Potatoes are cut into thin slices and heated with yeast, yields pressure at 140°-150°. Cell walls of plant tissues burst and starch

granules are exposed. The whole is thus converted into a mash. Hydrolysis is then effected with 'malt' or 'Mucor'.

Malt is barley seed germinated by soaking in water and keeping in a moist atmosphere at about 15°. During germination, an enzyme, *diastase* (amylase), is formed. Germination is arrested by heat, but the temperature should not be high enough to destroy the enzyme itself. Alternative sources of amylase are certain mould fungi, notably species of *Aspergillus* and *Mucor*. For the hydrolysis of rice in making the famous Japanese drink Saké, *Aspergillus oryzae* is used. Certain mucors are employed for producing industrial alcohol from starchy materials.

Malt in the British Isles and mucor in the continent are commonly used. (To the starchy mash of potato or cereal, malt is added and the temperature raised to 50°. Fermentation sets in and starch is converted mainly into maltose (or malt-sugar), a little dextrin; $(C_6H_{10}O_5)_n$ may also be formed. The hydrolytic enzyme, *diastase*, present in the malt brings about this change. The reaction is complete in about half-an-hour. The liquid is cooled to 15° and yeast added. Another hydrolytic enzyme, *maltase*, present in most yeasts, hydrolyses maltose to glucose which is finally fermented by *zymase* to alcohol. The temperature is maintained slightly above 30°; the operation requires about four days. The liquid is then distilled to obtain aqueous alcohol.



Starch can be hydrolysed to glucose also by warming with dilute H_2SO_4 , the liquid is neutralised with lime and fermented with yeast as usual. This is a simpler way but much of the starch is converted by side-reaction into unfermentable products.

Only a dilute solution of alcohol can be obtained by fermentation, for the yeast cell is killed when the concentration of alcohol reaches about 15%. The fermented liquor (wash) containing 8-10% alcohol is distilled in Coffey's still and by one operation, a spirit of 80-90% strength is obtained. The essential parts of a Coffey's still are two tall fractionating columns, known as analyser and rectifier, through which steam and alcohol pass in opposite directions. In the analyser, the steam takes away the alcohol vapour from the dilute alcohol, which condenses at the top of the rectifier and is sent to the receiver. This is called *rectified spirit*, containing 95.6% alcohol by weight. Besides alcohol, fusel oil, glycerol, acetaldehyde, succinic acid, acetone, etc., are also formed in varying amounts during fermentation. These are removed during fractionation. The yield of alcohol from starch is about 85% of the theoretical. In India alcohol for drinking is produced extensively by fermenting *mahwa* (*Bassia latifolia*) flowers which are rich in glucose and fructose.

Absolute alcohol (b.p. 78.5°) having no trace of water, cannot be obtained by fractionation as a constant-boiling (or azeotropic) mixture (b.p. 78.15°) with 4.43% of water is formed. If, however, it is distilled over fresh quicklime, alcohol containing about 0.3% of water is obtained. This is commonly known

as absolute alcohol. The last traces of water can be removed by distillation over requisite quantity of metallic magnesium or calcium and collecting in absence of moisture. Absolute alcohol is now in great demand as a commercial solvent. Alcohol is also dehydrated by adding benzene. Benzene, alcohol and water form a low-boiling ternary mixture (b.p. 65°); when this is driven off, a binary mixture of benzene and alcohol (b.p. 68.25°) goes next and finally absolute alcohol distils at 78.5° . The benzene is recovered and used again. Traces of water in alcohol may be detected by adding anhydrous copper sulphate (which turns blue), or calcium carbide (which produces acetylene gas).

Alcohol from molasses.—Molasses, the mother-syrup from the crystallisation of cane- or beet-sugar, contains sucrose (about 30%) and invert-sugar (nearly 32%). It is fermented to alcohol; the invertase of yeast converts the sucrose into invert sugar. The dark-coloured, thick liquid is diluted with water to make a 10% solution of sugar. A nutritive solution (e.g., ammonium sulphate) is added if sufficient yeast food is not already there. A little sulphuric acid retards bacterial action. The yeast thrives most vigorously in slightly acid solution. In wooden or enamelled iron vessels the liquid is mixed with yeast (5% by volume of the liquid) and maintained at 21° – 37.8° . Heat is evolved during fermentation which is complete in about 3 days. Under optimum conditions, 90% of the sugar is fermented in 36 hours.

The weak alcohol (7.8%) is rectified as usual to 95%. About 0.4 gallon of rectified spirit is obtained from a gallon of molasses. 101.37 lac gallons of power alcohol, 50.95 lac gallons of rectified spirit and 34.70 lac gallons of denatured spirit were produced from molasses in India during 1957. Ethylene for making polythene is derived from fermentation alcohol in India.

Bye-products of alcoholic fermentation.—The carbon dioxide is solidified into 'dry ice', and also used for making synthetic methanol. One ton of molasses yields on fermentation about 520 lb. of CO_2 . Tartar, the brown solid that separates during fermentation, is acid potassium tartrate, from which tartaric acid and Rochelle salt (q.v.) are made. **Fusel oil**, a bright yellow, oily liquid with nauseating odour, is the last runnings in the distillation of crude spirit. The chief constituent is iso-amyl alcohol or isobutyl carbinol, $(\text{CH}_3)_2\text{CH}-\text{CH}_2-\text{CH}_2\text{OH}$, (b.p. 131°); traces of two propyl alcohols, butyl alcohols, some esters, etc. are also present. It is worked up for amyl (Latin *amylum*, starch) alcohol, an industrial solvent. Fusel oil is formed by the action of yeast on certain amino-acids (such as valine and leucine) derived from proteins of starch. Its amount in raw spirit can be increased by adding leucine to the fermenting liquid. Normally, it is about 0.6% of the sugars fermented. Amyl acetate (oil of pears) is a valuable solvent for varnishes, it is also used in confectionery and fruit essences.

Alcoholic beverages.—These have different percentages of alcohol. There are two classes—distilled and undistilled. They contain colouring and flavouring materials besides a large proportion of water. Fortified wines e.g. port or sherry contain added alcohol. Dry wines have little or no sugar. Port, sherry, hock, claret, champagne, etc. are different varieties of wine.

Distilled			Undistilled		
Name	Source	% Alcohol	Name	Source	% Alcohol
Whisky	malt	35-40	Beer, ale	malt and hops	3-6
Rum	molasses	"	Wines	grape juice	8-12
Brandy or cognac	grape juice	40-50	Port, sherry	"	14-20
Gin	maize	about 50	Cider	apple juice	4-8

Alcohol gets oxidised in our system and supplies heat energy. It requires no digestion but its harmful effects outweigh its food value. In sufficient doses, it partially paralyses the nervous system and produces intoxication. It generally proves fatal when the concentration in the blood exceeds 0.6%.

Manufacture of beer.—Barley is moistened to germinate. The enzyme, diastase, thus formed hydrolyses the starch in barley to maltose and dextrin. By raising the temperature to 50°, germination is arrested. The sweet aqueous extract, called wort, is boiled with hops (which supplies a preservative, precipitates proteins and also gives a flavour), cooled to 30° and yeast added to it. Fermentation is continued until the concentration of alcohol in the liquid is about 5%. The resulting beer is filtered off and a little CO₂ may be added to it.

Methylated spirit is rectified spirit rendered unfit for drinking by adding poisonous and unpalatable substances, such as wood-spirit (about 10%), pyridine or mineral naphtha (a petroleum product), etc. Spirit is generally denatured in India by adding 0.5% light caoutchoucine (obtained by distilling vulcanised rubber) and 0.5% pyridine bases of guaranteed mineral origin. Methylated spirit is extensively used for making varnish and domestic purposes. It is duty-free.

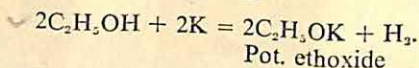
Power alcohol.—The petroleum resources of the world are likely to be exhausted soon even at the present rate of consumption. Synthetic petrol (p. 54) partly solves the problem. Alcohol is a motor fuel used with petrol and benzene, etc. Alcohol for the generation of power is known as power alcohol. Industrial rectified spirit does not mix with petrol but absolute alcohol does. A third component—ether, benzene or tetraline—is added if rectified spirit is used. In France, Germany, Italy, etc., mixing of 20-30% alcohol with petrol is compulsory. India's petroleum resources are very limited. Power alcohol from waste molasses saves petroleum; it is denatured with kerosene, benzene or petrol.

Proof spirit.—Alcohol and its preparations are taxed in all countries—in England the tax is £7, in U.S.A. \$40, and in India, about Rs. 70/- per gallon of absolute alcohol. The specific gravity of a sample being known, the p.c. of alcohol in it is obtained from standard tables. When alcohol mixes with water, the volume contracts. Excise people use hydrometers that read the p.c. of alcohol in terms of 'proof spirit'. Proof spirit is 57.1% alcohol (by volume) at 60°F and has a sp. gr. 0.91976 at 60°F. The strength of a liquor is expressed as degrees under or over proof, according as it is weaker or stronger than proof spirit. Thus 10° over proof means that 100 volumes of the liquid, diluted with water, will give 110 volumes of proof spirit; 10° under proof means that 100 volumes of the liquid contain as much alcohol as 90 volumes of proof spirit. The tax is levied on the basis of proof spirit. This determination of strength of alcohol goes by the name of alcoholmetry. Formerly, the strength was roughly determined by pouring alcohol over gunpowder and lighting it. If the gunpowder could be ignited after the alcohol had burnt away, it was taken as a proof that the alcohol did not contain too much water. Such alcohol was termed proof spirit; if the powder did not take fire, it was called under proof.

Properties.—Ethyl alcohol is a colourless, volatile liquid with a pleasant smell and a burning taste. It boils at 78.5° and has a specific gravity of 0.789 at 20°. It is miscible with water in all proportions with evolution of heat and contraction in volume. It freezes at -114° and so is used in thermometers for measuring low temperatures. Alcohol is a good solvent for many organic compounds, and has extensive use in pharmacy for making tinctures and extracts. It is highly hygroscopic; it burns with a pale blue flame. In small doses, alcohol is a good stimulant but in large quantities, it acts as a poison. Drinking, like opium eating, is habit-forming. It favours accumulation of unused fat in the body. Heated alone, alcohol remains unchanged upto 800°, but in presence of alumina, yields ethylene at about 360° (p. 58).

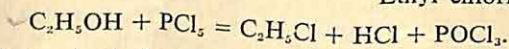
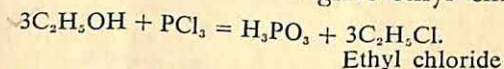
Uses.—Ethyl alcohol is employed for making methylated spirit (for varnishes, lacquers, etc.), ether, ethylene, chloroform, iodoform, acetic acid, etc. and also transparent soaps, hair washes, tinctures and tonics. Alcohol is required in the dye and rayon industries, it is a cheap solvent. Power alcohol is used in automobiles; it is also an antifreeze for radiators. Ethyl esters make fruit essences and perfumes. Alcoholic beverages are well known; its minor uses are for sterilisation in surgery, in spirit lamps, etc.

Reactions.—(1) Sodium or potassium dissolves in alcohol producing ethoxides (or alcoholates) and hydrogen:



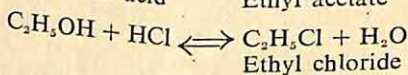
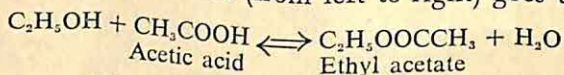
Metals above hydrogen in the electrochemical series liberate hydrogen from alcohol. Sodium ethoxide is an important catalyst. It is readily hydrolysed by water to $\text{C}_2\text{H}_5\text{OH}$ and NaOH ; ethanol is a very weak acid ($K_a = 7.4 \times 10^{-16}$).

(2) Phosphorus tri- or penta-chloride gives ethyl chloride:



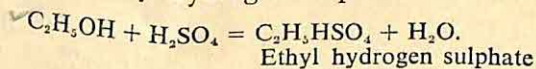
The solid, less volatile but more active, pentachloride is preferred to the trichloride. Thionyl chloride, SOCl_2 , in presence of pyridine, yields alkyl chlorides from alcohols in good yield.

(3) With acids, organic or inorganic, alcohol gives organic salts (or esters) and water. When the ionisable hydrogen of an acid is replaced by an alkyl radical, we get an **ester**. In presence of suitable dehydrating agents, the reaction (from left to right) goes to completion.

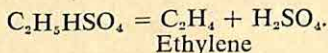
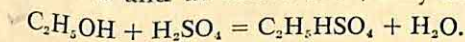


(4) Strong sulphuric acid reacts with alcohol in *three* ways:

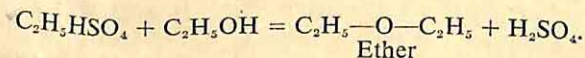
(i) At about 100° ethyl hydrogen sulphate is formed:



(ii) With excess *acid* and at about 165° , ethylene results (p. 57).

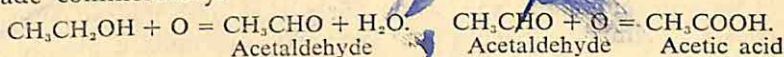


(iii) If the *alcohol* be in excess, we get ether at about 140° .

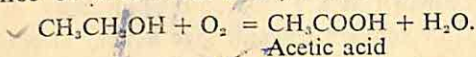


(5) Ethyl alcohol is oxidised to acetaldehyde by potassium dichromate and moderately strong sulphuric acid. If the reaction be

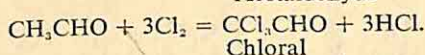
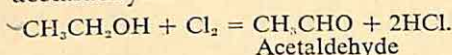
prolonged, we get acetic acid. The first step in the oxidation of a primary alcohol, RCH_2OH , is an aldehyde, RCHO . On passing alcohol vapour mixed with air over heated copper (at $200-300^\circ$), acetaldehyde is made commercially.



(6) If alcohol vapour and air be passed over heated platinised asbestos, acetic acid results. A dilute solution of the alcohol, exposed to air in presence of *bacterium aceti*, forms acetic acid.



(7) Chlorine oxidises ethyl alcohol to acetaldehyde; with excess of chlorine, chloral is produced. With excess of alcohol, acetal (p. 130) results from the acetaldehyde.

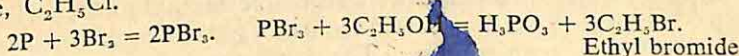


(8) On heating above 800° , ethanol decomposes into ethylene and water, and acetaldehyde and hydrogen.

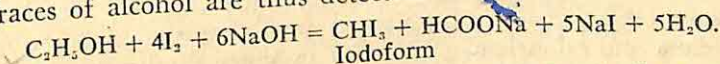
(9) Alcohol reacts with bleaching powder and water to form chloroform (p. 77).



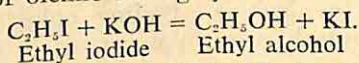
(10) With bromine (or iodine) and red phosphorus, we get ethyl bromide (or iodide) from alcohol (p. 72). PCl_3 similarly yields ethyl chloride, $\text{C}_2\text{H}_5\text{Cl}$.



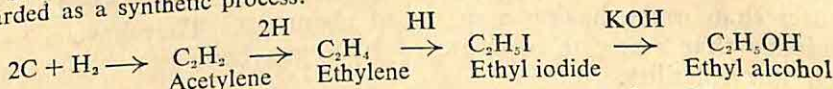
(11) Iodine and alkali give iodoform with ethyl alcohol (p. 79). Traces of alcohol are thus detected.



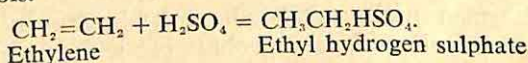
General methods of preparation.—(1) By boiling alkyl halides with aqueous caustic potash or treating them with moist silver oxide (p. 74). Formation of olefine is largely avoided in the latter case.

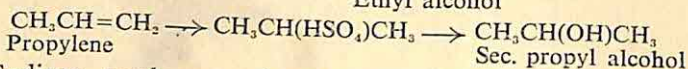
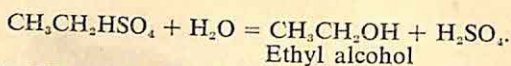


Since alkyl halides may be obtained directly from hydrocarbons, it may be regarded as a synthetic process:

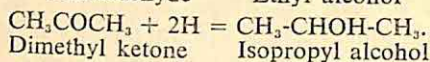
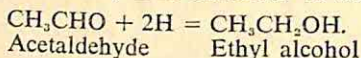


(2) By absorbing olefines in fuming sulphuric acid and hydrolysing the product (p. 59). Propylene and higher olefines yield secondary and tertiary alcohols.

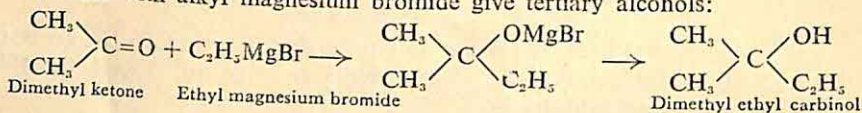




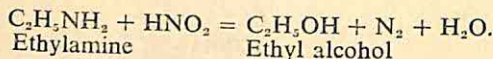
(3) Sodium amalgam and water, or nickel and hydrogen reduce aldehydes to primary alcohols, and ketones to secondary alcohols.



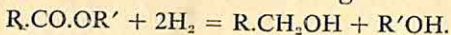
Ketones with alkyl magnesium bromide give tertiary alcohols:



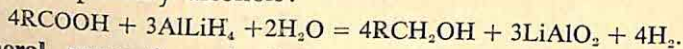
(4) Nitrous acid and primary alkyl amines, R-NH_2 , (q.v.) yield primary alcohols.



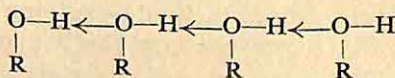
(5) By catalytic reduction of esters of higher fatty acids, higher alcohols are obtained. These are converted into sulphates, sodium salts of which $(\text{RO.SO}_3\text{Na})$ form a new class of detergents and wetting agents.



(6) Lithium aluminium hydride, LiAlH_4 , in ether solution reduces fatty acids to primary alcohols:

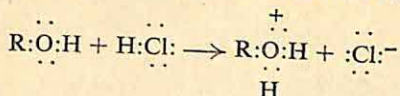


General properties.—As is characteristic in a homologous series, other aliphatic fatty alcohols closely resemble methyl and ethyl alcohol. They are colourless and neutral to litmus; the lower members are liquid at ordinary temperature. The consistency becomes oily as we go higher up in the series, and from $\text{C}_{12}\text{H}_{25}\text{OH}$, they are waxy solids. The lower alcohols possess a distinct taste and smell, $\text{C}_4\text{—C}_7$ members have unpleasant odour, $\text{C}_8\text{—C}_{12}$ have sweet smell but the higher ones are both tasteless and odourless. Solubility in water diminishes as the mol. wt. (or the hydrocarbon portion) increases—methyl, ethyl and propyl alcohols are miscible with water in all proportions, while $\text{C}_{16}\text{H}_{34}\text{O}$ is insoluble in water; the hydroxyl, —OH , is the solubilizing and functional group in alcohols. Boiling points of similarly constituted alcohols rise regularly with mol. wt. each $\text{—CH}_2\text{—}$ advancing the b.p. by about 20° . The b.p. of a primary alcohol, as a rule, is higher than that of an isomeric secondary or tertiary alcohol. Alcohols are lighter than water, having a sp. gr. of about 0.8. They have a lesser tendency than water to associate by hydrogen bonding; this explains their low volatility.



Alcohols react with metals above hydrogen in the electromotive series to produce *alkoxides* or alcoholates; with acids they form esters,

with phosphorus pentachloride they yield alkyl chlorides, and so on. Alcohols are difficult to reduce; they, however, form the corresponding alkanes on heating with strong HI and red phosphorus. Alcohols dissolve in strong acids forming oxonium salts like ethers (p. 121); they are more soluble in aqueous solutions of strong acids than in water due to the competition of alcohol and water mols. for the proton.



The alcohols, $\text{C}_n\text{H}_{2n+1}\text{OH}$.

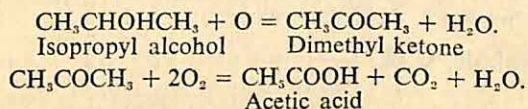
Name	Formula	b.p. °C.	Sp. gr. at 0°C	Solubility in water
Methyl alcohol,	CH_3OH	64.5	.814	Miscible
Ethyl alcohol,	$\text{C}_2\text{H}_5\text{OH}$	78.5	.806	"
<i>n</i> -Propyl alcohol,	$\text{C}_3\text{H}_7\text{OH}$	97	.817	"
Iso-propyl "	"	82	.786	"
<i>n</i> -Butyl alcohol,	$\text{C}_4\text{H}_9\text{OH}$	117	.823	1 : 12
Iso-butyl "	"	107	—	1 : 10
Sec. butyl "	"	99	.810	1 : 8
Tert. butyl "	"	83	.784	Miscible
<i>n</i> -Amyl alcohol	$\text{C}_5\text{H}_{11}\text{OH}$	137	.829	Insoluble
Iso-amyl "	"	131	.824	"
<i>n</i> -Hexyl alcohol,	$\text{C}_6\text{H}_{13}\text{OH}$	157	.833	"

Distinction between primary, secondary and tertiary alcohols

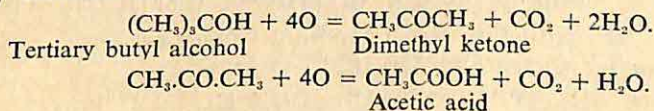
(i) By oxidation: (a) Primary alcohols yield first aldehydes and then acids, both having the *same* number of carbon atoms as the alcohols.



(b) Secondary alcohols form ketones with the *same* number of carbon atoms as the original alcohol but on further oxidation, give acids with a *fewer* carbon atoms:



(c) Tertiary alcohols form ketones with a *fewer* carbon atoms, and on further oxidation, acids with still fewer carbon are produced. Tertiary alcohols are difficult to oxidise.



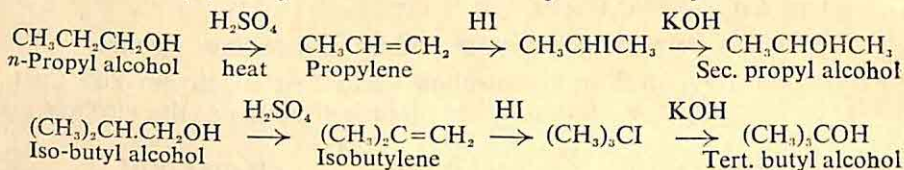
(ii) On passing the vapour over heated nickel, a primary alcohol gives an aldehyde and hydrogen, a secondary alcohol produces a ketone and hydrogen, while a tertiary alcohol yields an olefine and water.

(iii) In *Victor Meyer's method*, the alcohols are converted into corresponding alkyl iodides and then into nitro-paraffins (by distilling with silver nitrite). These are distinguished by their behaviour towards nitrous acid.

Alcohols	Nitro-paraffins	Reaction with HNO_2
$\text{R.CH}_2\text{OH}$ (Primary)	RCH_2NO_2 (Primary)	$\text{R.C} \begin{matrix} \nearrow \text{NO}_2 \\ \searrow \text{NOH} \end{matrix}$ Nitrolic acid With NaOH , it produces a dark-red salt.
R_1CHOHR_2 (Secondary)	$\text{R}_1\text{R}_2\text{CHNO}_2$ (Secondary)	$\text{R}_1 \searrow \text{C} \begin{matrix} \nearrow \text{NO} \\ \searrow \text{NO}_2 \end{matrix} \text{R}_2$ Pseudo-nitrol It gives a blue solution in alcohol and ether.
$\begin{matrix} \text{R}_1 \\ \text{R}_2 \end{matrix} \text{C(OH)R}_3$ (Tertiary)	$\begin{matrix} \text{R}_1 \\ \text{R}_2 \end{matrix} \text{C(NO}_2\text{)R}_3$ (Tertiary)	No reaction.

(iv) Tertiary alcohols decompose to olefines when warmed with zinc chloride, phosphorus pentoxide, etc. They are, however, practically inert towards sodium.

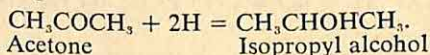
Conversion of primary into isomeric secondary and tertiary alcohols:



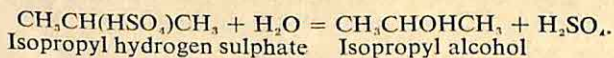
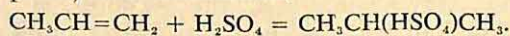
Tests for methyl and ethyl alcohol.—(1) Ethyl but not methyl alcohol responds to the iodoform test. (2) On warming with acidified dichromate, methyl alcohol gives formaldehyde and formic acid, while ethyl alcohol gives only acetaldehyde. (3) With salicylic acid and sulphuric acid, methyl alcohol produces a distinct odour of 'oil of winter-green'. (4) With an acetate and H_2SO_4 , ethyl alcohol gives the fruity odour of ethyl acetate.

Propyl alcohols, $\text{C}_3\text{H}_8\text{O}$.—Two are known; *n*-propyl alcohol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (b.p. 97°), obtained from fusel oil by fractional distillation, has little importance but isopropyl alcohol, $(\text{CH}_3)_2\text{CHOH}$ (b.p. 82°), is an industrial solvent used in place of ethyl alcohol as it is duty-free. Both are employed as antifreeze in automobile radiators, and are poisonous. Isopropyl alcohol or 'Petrolol' is prepared from:

(i) acetone by reduction with sodium amalgam or catalytic hydrogenation under pressure at $150\text{--}180^\circ$.

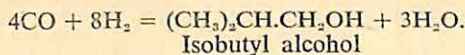


(ii) propylene, a bye-product of petroleum cracking, by the action of 85% sulphuric acid at $24\text{--}27^\circ$, followed by hydrolysis (cf., ethyl alcohol from ethylene, p. 59) and distillation.



Isopropyl alcohol is chiefly used in making acetone which is in great demand for explosives and plastics. It gives iodoform test (p. 93) and finds use in shaving lotions, nail polish, etc.

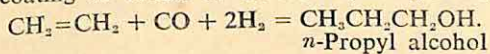
Butyl alcohols, C_4H_9OH .—Of the four isomers, *normal butanol*, $CH_3CH_2CH_2CH_2OH$, (b.p. 117°) is an important solvent; it is formed in large quantities (about 60%) with acetone and ethanol during the fermentation of starchy materials such as rice, wheat, corn, etc. with *C. acetobutylicum*. These are separated by fractional distillation. *n*-Butanol is also made by reducing crotonaldehyde, $CH_3CH:CHCHO$, obtained from acetaldehyde (p. 132). Butanol and its acetate are solvents for quick-drying nitro-cellulose paints and lacquers. Butyl acetate is a fruit essence. *Isobutyl alcohol*, $(CH_3)_2CH.CH_2OH$, (b.p. 108°) occurs in fusel oil; it is made by Fischer-Tropsch process using nickel catalyst; it is a lacquer solvent and also used in making synthetic musk.



Sec. butanol, $CH_3CH_2CHOHCH_3$, (b.p. 99°) is made from *n*-butylenes of cracked petroleum by hydration with H_2SO_4 . It is a solvent for lacquer, gums and shellac. *Tert. butanol*, $(CH_3)_3COH$, (b.p. 83°) is obtained likewise from isobutylene; it has limited use as a solvent. Unlike its isomers, it is completely miscible with water. Methyl ethyl ketone (M.E.K.), a valuable solvent, is made from *sec.* butanol by dehydrogenation.

Amyl alcohols, $C_5H_{11}OH$.—Of the eight isomers, two primary amyl alcohols, *viz.*, isobutyl carbinol, $CH_3CH(CH_3)CH_2CH_2OH$ (b.p. 131°) and active amyl alcohol, $CH_3CH_2CH(CH_3)CH_2OH$ (b.p. 128°) occur in fusel oil (p. 90) and are isolated therefrom for making amyl acetate, a solvent for nitro-cellulose lacquers. Normal and iso-pentane of casinghead gas are chlorinated in the dark at 200° , the resulting mono-chloropentanes are hydrolysed with aqueous NaOH in presence of sodium stearate to a mixture of amyl alcohols (*pentasol*) which are made into amyl acetate.

During the last war Germany made alcohols and aldehydes by passing an olefine, carbon monoxide and hydrogen under pressure (150-300 atmos.) over pumice having a coating of cobalt at $150-200^\circ$ (oxo process).



Many higher alcohols occur as esters in nature. Thus spermaceti wax, from the head of sperm-whale, is an ester of cetyl alcohol, $C_{26}H_{53}OH$ (m.p. 49°) used in face creams. Chinese wax is an ester of ceryl alcohol, $C_{26}H_{53}OH$; while myricyl alcohol, $C_{31}H_{63}OH$ occurs in bees wax.

QUESTIONS

1. Write the structural formulæ of the isomeric alcohols having the molecular formula, $C_4H_{10}O$. By what reactions can these compounds be distinguished?—B.Sc., London, 1928.

2. Starting with acetylene, outline a possible synthesis of (a) ethyl alcohol (b) tertiary butyl alcohol.—B.Sc., Punjab, 1932.

3. Write equations for reactions by which primary, secondary and tertiary alcohols can be prepared. Describe one method, other than oxidation method, by which different types of alcohols can be distinguished.—B.Sc., Punjab, 1933.

4. Give an account of the various processes concerned in the preparation of alcohol from starch.—B.Sc., Punjab, 1933.

~~5.~~ How is absolute alcohol prepared?—B.Sc., Bombay University, 1933.

6. What is the relation between alcohols and aldehydes? How would you obtain one class from the other? By what reactions can one distinguish between a primary, a secondary, and a tertiary alcohol?—B.Sc. Pass. Dacca University, 1938.

7. How is absolute ethyl alcohol prepared on a technical scale? Mention its uses. Starting with ethyl alcohol, indicate how the following substances are prepared: (a) diethyl ether, (b) ethyl acetate, (c) iodoform, and (d) ethylene.—B.Sc., Degree Exam., 1942, Annamalai Uni.

8. Describe the manufacture of ethyl alcohol. How is the constitution of this substance established?—B.A. & B.Sc., Degree Exam., 1942, Andhra University.

9. Describe the preparation and properties of methyl alcohol. How is it distinguished from ethyl alcohol?—B.A. & B.Sc., Degree Exam., 1934, Andhra University.

CHAPTER IX

MECHANISM OF ORGANIC REACTIONS

Our current ideas about atomic structure and the nature of chemical bonds enable us to have a clearer understanding of the course and rate of chemical reactions. We shall briefly discuss here how the electronic theory of valency explains fairly satisfactorily the mechanism (*i.e.*, the route by which a reaction proceeds) of many organic reactions. The vast majority of reactions of organic molecules, consisting of atoms linked by covalent bonds, involve the rupture and re-formation of such bonds. A covalent bond in a neutral molecule $A:B$ may break in two ways, *viz.*, (i) by a symmetrical dissociation into neutral atoms or radicals, each retaining one of the electrons of the original shared duplet, *e.g.*,



or (ii) by an unsymmetrical dissociation into ions involving the transfer of a duplet as a whole to one or other of the atoms which were bound by the duplet, *e.g.*,



The first type of bond fission is called *homolytic*; fragments $A\cdot$ and $B\cdot$ are atoms or free radicals. Mechanisms in which bonds break by this process are, therefore, known as *free radical mechanisms*. Reactions in the gas phase and those catalysed by free radicals are generally explained by this mechanism.

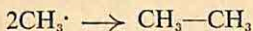
Free radical mechanism.—It has been shown that during thermal or photo-chemical decomposition of some organic compounds in the vapour phase, electrically neutral fragments—atoms or radicals—are formed but no charged ions. Due to the presence of unpaired electron in them they are highly reactive, so much so that they exist only transitorily in chain reactions. Two such atoms or free radicals unite, on collision, to form a molecule. Some examples are given below.

(i) *Pyrolysis of hydrocarbons.*—Ethane, CH_3-CH_3 , decomposes at high temperature by homolytic fission into two free methyl radicals, $2CH_3\cdot$ which react in either of the following ways:

(a) Abstract hydrogen from a molecule of ethane:



(b) Reunite to form back ethane in presence of a third molecule (wall of the containing vessel, for example) which absorbs the energy thus set free:

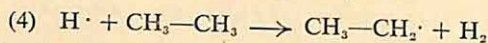
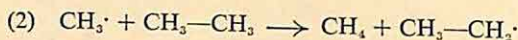


(c) Form ethylene by disproportionation:

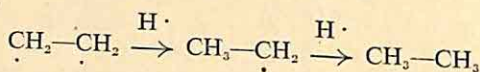
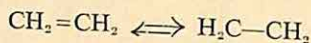
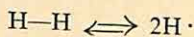


The overall picture of the chain reaction may be depicted as



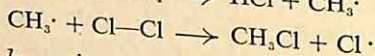


(ii) *Catalytic reduction*.—During catalytic hydrogenation in presence of finely divided nickel, platinum or palladium, molecules are believed to be adsorbed on the surface and dissociate into atoms or free radicals. They may have an unshared electron or there may be two unshared electrons due to a rupture of the double bond giving rise to diradicals. The catalytic reduction of ethylene with hydrogen may be represented as

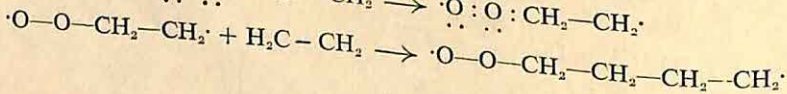
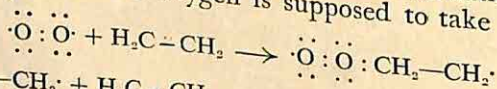


Atoms of hydrogen and free ethylene diradicals are stabilised by weak pairing of their unshared electrons with the electrons of the metal surface, a monomolecular layer is thus formed. Ethane is produced by a collision between a hydrogen atom and a diradical.

(iii) *Thermal or photo-chemical halogenation*.—At high temperature or at ordinary temperature in presence of light, chlorine or bromine reacts with a paraffin, replacing a hydrogen in the form of halogen acid (p. 43). Here heat or light dissociates a halogen molecule into atoms which collide against hydrocarbon molecules producing hydrocarbon radicals and hydrogen halide. The free radicals in their turn then collide with halogen molecules forming alkyl halide and more halogen atoms. And the *chain reaction* continues following the same pattern. Methane and chlorine react as



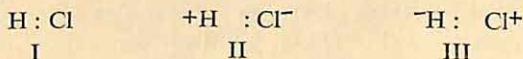
(iv) *Catalytic polymerisation*.—The oxygen molecule which has two unpaired electrons is believed to behave to some extent as a free radical. During polymerisation catalysed by oxygen, it probably unites with one carbon atom of the compound forming a double bond by taking one electron, the electron on the other carbon atom remaining free. This 'free radical' now combines with another molecule of the unsaturated compound in a similar manner, leaving a free electron on the other carbon of the double bond. This chain reaction goes on until the chain is broken by the combination of two free radicals. Polymerisation of ethylene to polythene in presence of oxygen is supposed to take place as



Reactions following free radical mechanism may be induced by introducing small amounts of known free radicals, and arrested either by fairly stable free radicals or substances that combine with free radicals to form stable ones.

Ionic mechanism.—The second type of bond fission (p. 99) is known as *ionic* or *heterolytic*; it occurs due to the partial ionic nature of the covalent bond. In case the two atoms forming a covalent bond are identical, as in the hydrogen molecule, no net separation of charge within the molecule is possible inasmuch as the polarity of the one balances that of the other. If they have different affinities for electrons, one has a tendency to accept, and the other to donate, an electron. In such cases, heterolytic fission may occur and the fragments would be either A^+ and $:B^-$ or $:A^-$ and B^+ i.e., two ions, were such existence possible. Mechanisms involving such bond fission during reaction are called *ionic* or *polar mechanisms*, by which most organic reactions are believed to occur. Reactions in liquid phase wherein polar molecules or ions take part, are evidently polar reactions. A positive group containing a carbon atom that has a pair of electrons less in its valence shell as a result of heterolytic fission, is called *carbonium ion* while a negative group with a carbon atom that has an unshared pair of electrons, also a product of ionic fission, is known as *carbanion*.

In hydrogen chloride, chlorine has a greater affinity for electrons than hydrogen; hence the electron pair of the covalent bond between them are displaced permanently towards chlorine appreciably. As a result, chlorine acquires a small negative charge and hydrogen a small positive charge. Of the three possible structures for hydrogen chloride,

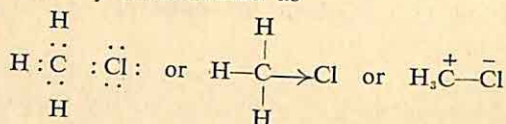


II is, therefore, a closer approximation. Alkyl halides such as ethyl iodide, $\text{C}_2\text{H}_5\text{I}$, undergo double decomposition more or less like inorganic salts (pp. 73-75), the iodine being displaced as negative iodide ion, e.g.,



Between the truly covalent bond as in $A\text{—}B$ when A and B are identical (for example, the bond in the hydrogen molecule, which is 100% covalent) and the truly ionic bond when A and B are radically different (as in potassium chloride, which is 100% ionic), there are numerous intermediate cases of partially ionic and partially covalent types, depending on the relative electronegativities of A and B (electronegativity is the tendency of an atom to attract electrons to itself when it is present as a part of an electron pair bond). Different atoms and radicals have different powers to attract electrons; for example, this power increases in the order: $-\text{C}_2\text{H}_5$, $-\text{CH}_3$, H , $-\text{C}_6\text{H}_5$, $-\text{OCH}_3$, I , Br , Cl , F , $-\text{NO}_2$. The displaced electrons, however, remain in the same valency shells. The displace-

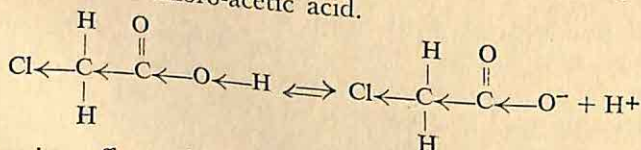
ment of electrons in methyl chloride, CH_3Cl , which is similar to hydrogen chloride, may be indicated as



the arrowhead which should not be confused with that indicating a dative bond (p. 37), shows the shifting of electrons towards the chlorine atom from a condition of equal sharing. If this chlorine occurs at the end of a carbon chain, its effect may be propagated to a distant atom in the chain; the intensity, however, diminishes rapidly as the distance increases. This is known as *inductive effect*. The chloro-acetic acids may be taken for illustration. When chlorine replaces a hydrogen of the methyl group in acetic acid, CH_3COOH , the ionisation constant (or strength) of the monochloro-acetic acid formed increases considerably. The ionisation or dissociation constants, K_a , for di- and tri-chloroacetic acids are increasingly greater:

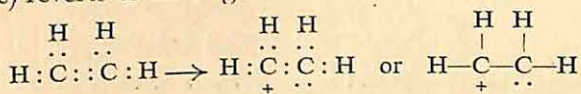
		K_a
Acetic acid,	CH_3COOH	1.86×10^{-5}
Monochloro-acetic acid,	CH_2ClCOOH	1.55×10^{-3}
Dichloro-acetic acid,	CHCl_2COOH	5.14×10^{-2}
Trichloro-acetic acid,	CCl_3COOH	1.21×10^{-1}

This increase in dissociation constant may be satisfactorily explained by the inductive effect of electronegative chlorine. Chlorine in monochloro-acetic acid attracts electrons from the carbon atom to which it is attached, towards itself. This renders the other carbon atom containing the hydroxyl group more positive; this in turn attracts electrons away from the oxygen of the $-\text{OH}$ group, which thus becomes more positive than in acetic acid. This then attracts electrons from the ionisable (*i.e.*, acidic) hydrogen allowing it to escape as proton. The oxygen of the $-\text{OH}$ group being now more positive, has less tendency to recombine with the proton set free. The result is a greater dissociation of mono-chloro-acetic acid.

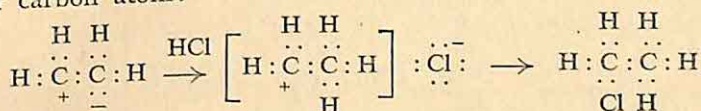


This inductive effect of chlorine further increases when the second and the third hydrogen atom of the methyl group are also replaced by chlorine. Such displacement of electrons may occur in another way. When ethylene, $\text{CH}_2=\text{CH}_2$, reacts with HCl to give ethyl chloride, $\text{CH}_3\text{CH}_2\text{Cl}$, it acquires a polar structure on the approach of the HCl molecule by a temporary but complete shift of electrons from one carbon atom to another. The action is almost instantaneous and, on

removing the attacking agent (HCl in this case) the charged molecule (here ethylene) reverts to its original state.



The hydrogen of HCl adds to the carbon having the displaced electron pair as hydrogen ion, and the negative chloride ion goes to the other carbon atom:

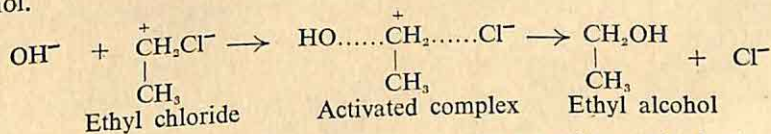


This shifting of electrons from one carbon to another on the approach of a reagent is called *electromeric effect* which is time-variable, i.e., not permanent, and is usually represented by a curved arrow. It is characteristic of addition reactions of unsaturated compounds. In the above case, the hydrogen ion which attracts electrons, is called *electrophilic* (electron loving); a point of low electron density in a molecule has affinity for electrons and is, therefore, electrophilic. Conversely, a point of high electron density in a molecule is known as *nucleophilic* (nucleus loving). In the above reaction, ethylene is nucleophilic as it attracts hydrogen ion which is deficient in electron. Many organic reactions take place on bringing together the electrophilic centre of one molecule and the nucleophilic centre of another. The following examples of ionic mechanism are typical:

(i) *Hydrolysis of alkyl halides*.—On refluxing alkyl halides with aqueous KOH, corresponding alcohols are formed by hydrolysis (p. 74).

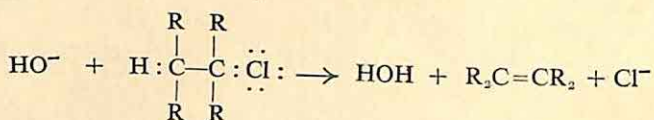


On the approach of the OH^- ion towards the carbon to which the halogen is attached, further shifting of electrons from this carbon atom towards chlorine occurs. This results in the partial formation of a new bond with the simultaneous weakening of the carbon-halogen bond. The nucleophilic OH^- ion then attaches itself to the carbon having low electron density in this activated complex, and the halogen is eliminated as a halide ion. The result is the formation of alcohol.

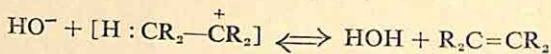
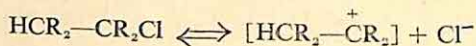


(ii) *Removal of halogen acid from an alkyl halide*.—Alcoholic KOH removes a molecule of halogen hydracid from an alkyl halide and an olefine is thus formed (p. 74). Here the OH^- ion extracts a proton from the β -carbon atom and simultaneously the halide ion is eliminated with the formation of a double bond between the two carbon atoms

by the pair of electrons released by the proton. The reaction is thus bimolecular.

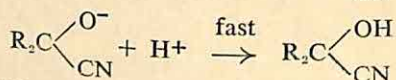
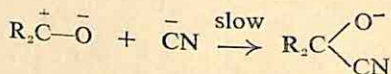


In the second mechanism which is unimolecular, ionisation of the halogen occurs first, the carbonium ion then combines with the OH^- ion to form an olefine and water:



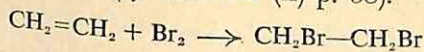
(iii) *Addition of hydrogen cyanide to a ketone, R_2CO .*—Ketones, R.CO.R , react with HCN to form an additive product, $\text{R}_2\text{C} \begin{smallmatrix} \text{OH} \\ \text{CN} \end{smallmatrix}$

In the ketone molecule, there is a nucleophilic centre on the oxygen atom and an electrophilic centre on the carbonyl carbon: $\text{R}_2\text{C}^+\text{O}^-$. During reaction with HCN , the nucleophilic cyanide ion which is the reactant here, attacks the carbonyl carbon:



Based on this reaction, ketones are electrophilic reagents while HCN is a nucleophilic one. That it is the CN^- ion which is added to the ketone and not HCN directly, follows from the fact that the velocity of the reaction is accelerated by alkali or salts of weak acids but retarded by acids and unaffected by neutral salts.

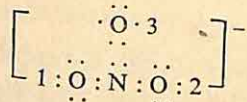
(iv) *Addition of halogen to olefines.*—Ethylene adds up bromine to give ethylene dibromide (cf. reaction (ii) p. 58).



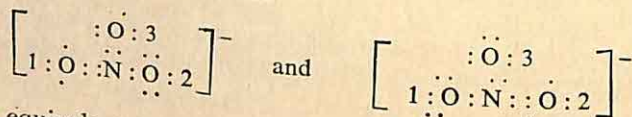
The ionic character of the reaction is evident from (i) the addition does not take place in gas phase, (ii) bromine vapour and ethylene gas combine only at the polar surface of the reaction vessel; the reaction is about thirty times faster when this surface is coated with a polar compound such as stearic acid than with a coating of non-polar paraffin wax. The reaction takes place stepwise inasmuch as when ethylene and bromine react in a neutral solution of NaCl , ethylene dibromide and α -chloro- β -bromo-ethane, $\text{ClCH}_2-\text{CH}_2\text{Br}$, are obtained and no trace of ethylene dichloride, $\text{ClCH}_2-\text{CH}_2\text{Cl}$. Evidently the chloride ion from NaCl solution gives with bromine the chloro-bromo compound from ethylene, but it cannot alone react with ethylene. Logically, therefore, bromine first reacts with ethylene to form an intermediate product

the mechanism of reaction in the two cases should, therefore, be different. For example, addition of HBr to propylene, $\text{CH}_3-\text{CH}_2=\text{CH}_2$, with pure reagents and in absence of air, is a polar or ionic reaction, initiated by a proton; the negative bromine attaches itself to the middle carbon atom and gives $\text{CH}_3-\text{CHBr}-\text{CH}_3$, following Markownikoff's Rule (p. 62). In presence of air or peroxides, propylene and HBr react at a much faster rate to form $\text{CH}_3-\text{CH}_2-\text{CH}_2\text{Br}$, a quite different product. This is a self-propagating chain reaction, following a free radical mechanism, which involves atomic bromine set free from HBr by a free radical produced by the homolytic fission of the peroxide (p. 62). The free bromine atom functions as an electrophilic reagent, attaching itself to the end carbon atom of higher electron density.

Mesomerism or resonance.—It is expected that the valence bond structure of a molecule should adequately express its properties. In many cases, however, a single structure fails to do that. For example, the nitrate ion, NO_3^- , is usually written as

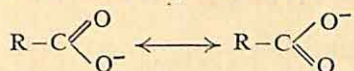


in which a single bond occurs between N and O(1) and another between N and O(2); in one each atom furnishes one electron while the other is a co-ordinate bond, both electrons being furnished by N. These bonds are apparently similar. But the bond between N and O(3) is a double bond, formed by two electrons from each atom. Since all the three oxygen atoms in the nitrate ion have been shown to be equivalent, all the nitrogen-oxygen bonds should be identical, *i.e.*, of the same type. The above structure does not indicate this. Two other possible structures for the nitrate ion are



which are equivalent to the first electronic structure, all containing the same number of unpaired electrons. According to the resonance theory, a structure, intermediate among these three, a sort of a hybrid, represents the true state of the nitrate ion; neither of them can do that singly. It is not possible to represent this intermediate state truly on the paper. In the three structures noted above, a double bond occurs between the nitrogen atom and one of the oxygen atoms in each case. Since all nitrogen-oxygen bonds are equivalent, none of these is a double bond, none is a single also. Each is, therefore, a hybrid type of bond, intermediate between a single and a double bond; or one might say, each has a one-third double bond character. Resonance lowers the energy content of a molecule (or an ion, or a radical) and makes it more stable than it would be otherwise. In resonance all the contributing structures must have the same number of unpaired electrons, the average positions of the electrons in them should not be very much different, and the only difference between these structures is the

difference in the positions of the electrons. Measurement of bond length values by X-ray diffraction in resonance hybrids supports the theory of resonance. For example, the carbon to oxygen distance in a carboxylate ion which has a hybrid structure,



is the *same* for both the oxygen atoms, being 1.27Å. This is intermediate between the interatomic distances for a double bond (1.21Å) and a single bond (1.42Å) between carbon and oxygen. In other words, neither of the carbon-oxygen bonds in it is a single bond or a double bond. It may be noted that resonance is possible only if the atoms involved are coplanar or nearly so. We shall come across many such cases of resonance structure amongst organic compounds. Whenever the actual normal state of a molecule cannot be adequately represented by any of the possible alternate structures which differ only in the positions of their valency electrons, the number of unpaired electrons remaining constant, the molecule is said to be resonating between these valence bond structures. Such a molecule is said to have a *meso-meric* (i.e., "between the parts" or intermediate) *structure*. The theory of resonance has proved very useful in elucidating the mechanism of many organic reactions and also for explaining the behaviour of numerous organic compounds.

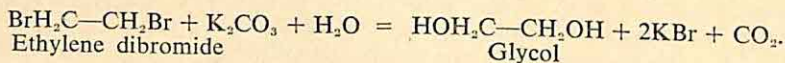
CHAPTER X

THE POLYHYDRIC ALCOHOLS

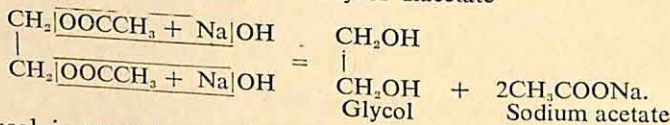
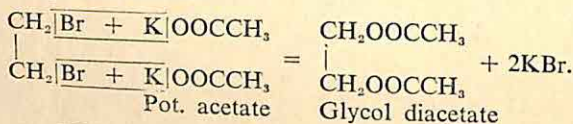
Of the compounds with more than one alcoholic hydroxyl group, the dihydric alcohol, glycol and the trihydric alcohol, glycerol are commercially important. Carbohydrates (Chapter XXVII) contain many such hydroxyl groups.

Dihydric alcohols, $C_nH_{2n}(OH)_2$.—The simplest member, methylene alcohol, $CH_2(OH)_2$, is unknown; two hydroxyl groups attached to the *same* carbon atom make the compound unstable and water is eliminated (p. 83). The next, ethylene glycol, $CH_2(OH)CH_2(OH)$, is representative of the series. Glycol means ethylene glycol, and the term *glycols* stands for the series.

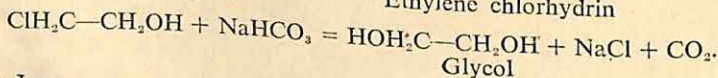
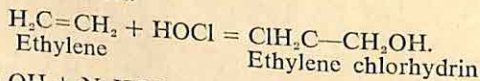
Glycol, CH_2OH-CH_2OH , is obtained in the laboratory by boiling under reflux ethylene dibromide with a dilute solution of potassium carbonate.



The aqueous solution is evaporated on water-bath and glycol extracted with ether-alcohol mixture from the semi-solid residue. By distilling off the solvents, glycol (b.p. 197°) is obtained. The reaction proceeds slowly, and the yield is poor due to side-reactions. A better method is to use potassium acetate and hydrolyse the product with dilute caustic soda. Wurtz first obtained glycol in 1856 from silver acetate and ethylene iodide.

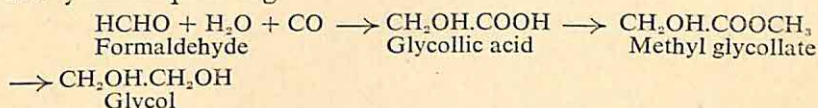


(2) Glycol is manufactured from ethylene (obtained from cracked oil, coke-oven gas, or by catalytic dehydration of ethyl alcohol) and hypochlorous acid (e.g., from bleaching powder and CO_2) at about 0° . Ethylene chlorhydrin formed is hydrolysed to glycol at 70° with dilute sodium bicarbonate solution.



(3) In a recent process formaldehyde, steam and carbon monoxide are heated at 200° under 700 atmospheres to get glycollic acid; this is esterified with methanol and the ester finally reduced to glycol with

H₂ at 200° under 30 atmospheres in presence of chromite catalyst. The yield is quite high.

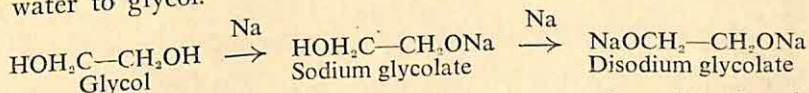


(4) More cheaply, ethylene oxide (made from ethylene and air) is hydrolysed to glycol (p. 110).

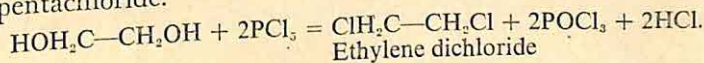
(5) Glycol results on passing ethylene into a dilute, alkaline solution of potassium permanganate in the cold (p. 59). But this is only of academic interest.

Properties and uses.—Glycol is a sweet (but toxic), syrupy liquid, extremely hygroscopic and without odour. It is heavier than ethyl alcohol (sp. gr. 1.127 at 15°) and has also a higher boiling point (197°). It is miscible with water or alcohol in all proportions but insoluble in ether. Glycol melts at -11.5°; it is, therefore, largely used as an anti-freeze in motor car radiators in cold countries. A 60% aqueous solution freezes at -49°. Glycol is also a solvent and a preservative. Its dinitro derivative is an explosive used with trinitroglycerine. In commerce, glycol is employed as a substitute for glycerine but not in pharmaceutical preparations as it is oxidised to poisonous oxalic acid, HOOC-COOH. For its high b.p., it is used for cooling airplane engines instead of water; it aids penetration of dyes, and facilitates wool spinning as a lubricant. Monoethyl ether of ethylene glycol, CH₂OH.CH₂OC₂H₅, or *cellosolve* is a solvent for cellulose nitrate. Certain alkyd resins (esters of glycol and dibasic acids) are made from glycol. In chemical properties glycol resembles alcohol; as it contains two primary alcoholic groups, the alcoholic characteristics are more intense. By catalytic polymerisation, glycol forms water-soluble, greasy solids used as lubricants and ointment bases. *Dacron* (or *Terylene*), a synthetic fibre, is made from glycol terephthalate.

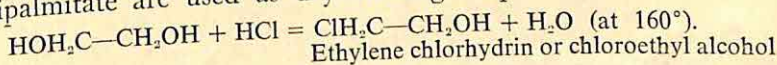
Reactions.—(1) Sodium (or potassium) replaces the hydrogen of the -OH group one by one. Sodium glycolate forms at low temperature and the disodium derivative at about 160°. Both are readily decomposed by water to glycol.



(2) Like ethyl alcohol, glycols give chloro-paraffins with phosphorus tri- or pentachloride.



(3) With acids, esters result (cf. alcohol, p. 92). Glycol dioleate and dipalmitate are used as dry-cleaning soaps.



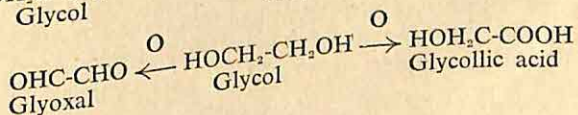
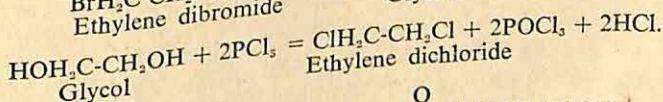
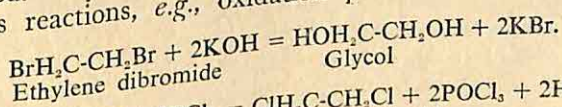
In these additive reactions, it behaves as an unsaturated compound, $\text{CH}_2=\text{CHOH}$, but since ethylene oxide gives ethylene dichloride, $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$, with PCl_5 , the cyclic structure has been accepted. With ammonia, di- and tri-ethanolamines, $\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$ and $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$, are also formed. With fatty acids, these form practically neutral soaps many of which, being soluble in both oil and water, are employed in dry-cleaning and 'cleansing creams'. Ethylene oxide is dehydrated glycol, elements of water having been removed from two OH groups of the same molecule. Such compounds are called 'inner ethers'. Mixed with 10% CO_2 , ethylene oxide is a fumigant for tobacco, cereals, etc. under the trade-name T-gas or Etox. CO_2 makes the vapours non-inflammable and non-explosive; ethylene oxide is non-toxic to man. It produces organic effect on cotton, and is largely converted into glycol by hydrolysis. U.S.A. made 1060 million lb. of ethylene oxide in 1957.

Glyoxal, OHC-CHO , a dialdehyde, is produced by oxidising glycol with nitric acid under suitable conditions, or ethylene with selenium oxide, SeO_2 . On distilling the reaction mixture, glyoxal goes off as a yellowish green gas which condenses to a yellow liquid (b.p. 51°). It is unstable and readily polymerises. Glyoxal is the simplest coloured compound of carbon, hydrogen and oxygen. It may also be obtained by careful oxidation of acetaldehyde, CH_3CHO , with nitric acid. Glyoxal is slightly soluble in water but readily soluble in alcohol or ether. It forms glycollic acid by Cannizzaro reaction (p. 130).

Dioxan or diethylene dioxide, $\text{O} \begin{array}{c} \text{CH}_2-\text{CH}_2 \\ \text{CH}_2-\text{CH}_2 \end{array} \text{O}$, is obtained by

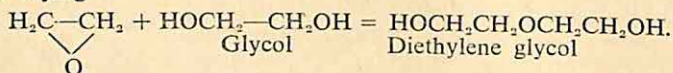
distilling glycol with 4% aqueous H_2SO_4 or phosphoric acid; it is an industrial solvent for cellulose acetate, resins, fatty oils, etc. It is an oily, pleasant smelling but toxic liquid (b.p. 102°), miscible with water and most organic solvents. Dioxan (m.p. 11°), is a solvent for the determination of mol. wts. by cryoscopic method. 80% dioxan forms an azeotropic mixture (b.p. 87°) with water. It is isomeric with ethyl acetate, and fairly toxic.

Structure of glycol.—The molecular formula of glycol is $\text{C}_2\text{H}_6\text{O}_2$. Sodium replaces two hydrogen atoms and phosphorus pentachloride gives ethylene dichloride, $\text{C}_2\text{H}_4\text{Cl}_2$. Hence, it has two $-\text{OH}$ groups. Its formation from ethylene dibromide shows that the two carbons are directly linked. Glycol is, therefore, $\text{CH}_2\text{OH}-\text{CH}_2\text{OH}$, which is supported by its reactions, e.g., oxidation products.

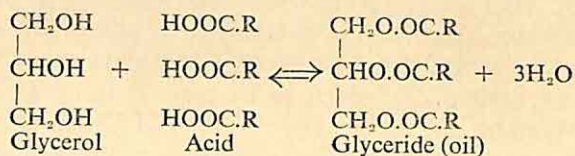


If glycol was $\text{CH}_3-\text{CH}(\text{OH})_2$, on oxidation it would yield acetic acid, CH_3COOH .

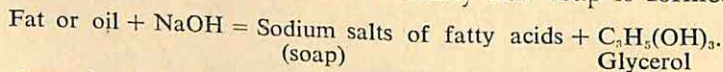
Diethylene glycol, made by heating glycol with ethylene oxide, is a lubricant in wool spinning and a solvent for dyes; it is added to the size for textiles to prevent drying.



Trihydric alcohols.—Of these, by far the most important is glycerol or glycerine, $\text{CH}_2\text{OH}.\text{CHOH}.\text{CH}_2\text{OH}$, first obtained in 1779 by the Swedish apothecary, Scheele by heating olive oil with litharge. In 1811, Chevreul (1786-1889) showed it to be a common constituent of *all* animal and vegetable oils and fats, e.g., cocoanut oil, olive oil, palm oil, tallow, lard, cod-liver oil, etc. and named it glycerol. Natural fats and oils are esters of glycerol with acids such as palmitic acid, $\text{C}_{15}\text{H}_{31}\text{COOH}$, stearic acid, $\text{C}_{17}\text{H}_{35}\text{COOH}$, oleic acid, $\text{C}_{17}\text{H}_{33}\text{COOH}$, etc. These are, therefore, called *glycerides*. Chemically, the formation of an oil may be represented as



Three mols. of fatty acids, same or different, may esterify a glycerine molecule, giving a simple or mixed glyceride respectively. Natural fats and oils seldom consist of a pure tri-glyceride. Oils and fats, on hydrolysis, give back fatty acids (mostly insoluble in water) and glycerol (miscible with water in all proportions). This may be effected with hot caustic alkalis, alkali salts of fatty acids are thus obtained. Sodium or potassium salts of fatty acids are the soaps of our daily use; this method of hydrolysis, better known as *saponification* (Latin *sapo*, soap), is the common way of making soap. As early as 1816 Chevreul established clearly how soap is formed.



Soap is slightly soluble in water, and is precipitated by adding common salt in excess. The liquor that is left behind is known as *spent lye* which contains 5-8% of glycerol.

Manufacture of glycerol.—(i) *From soap lyes:* Besides much water and some glycerol, the spent lye contains sodium chloride, free alkali, fatty and protein matters. To the lye acidified with HCl , aluminium sulphate is added. The fatty acids and soap in solution are precipitated as aluminium soap. These are filtered off. The filtrate, made slightly alkaline, is concentrated when common salt partially separates. As impure glycerine decomposes below its boiling point, evaporation is carried out under low pressure with two or more evaporators in series to economise heat; the salt is removed without stopping

evaporation. The evaporation is continued until the concentration of glycerol reaches about 80% (and that of common salt 10%). The liquid is decolorised with activated charcoal. Crude glycerine is purified by distilling under reduced pressure in a current of super-heated steam. The distillate is dehydrated by concentrating in vacuum pans as before. The straw-coloured glycerine thus obtained (99·8–99·9%) is good enough for dynamite. Colourless glycerine for scientific and medicinal purposes is obtained by treating it with bone charcoal, filtering and re-distilling the filtrate. Ionic impurities like NaCl, etc. are removed from soap lye by passing it through cation-anion exchangers (synthetic resin beds). Vacuum evaporation of the de-ionised product yields 95–99% glycerine.

(ii) *From 'sweet water'*: Mixed with paraffin wax, fatty acids (mainly stearic acid) make candles. Solid fats are, for this purpose, hydrolysed with dilute sulphuric acid under pressure. Solid fatty acids are removed; the mother-liquor, called *sweet water*, is neutralised and glycerine obtained therefrom as above.

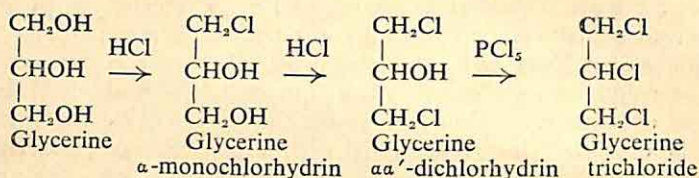
(iii) *From sugars by fermentation*: Alcoholic fermentation yields about 3% glycerol (p. 89). During the war of 1914–18 Germany got no oil-seeds from outside; she made glycerine from sugars by fermentation with yeast. Neuberg (1912) showed that in presence of sodium sulphite, the yield of glycerine rose up to 25%; the yield of alcohol fell considerably, some acetaldehyde being produced. Germany thus made 1,000 tons of glycerine per month for explosives. A 36% yield of glycerol has been reported with sulphite and sugar in the ratio 2:1. Sodium carbonate also increases the yield of glycerol but it cannot suppress undesirable bacteria like the sulphite.

Glycerine in India: Soap factories around Calcutta mostly throw away the spent lye. As glycerine is largely used for explosives, its peace-time demand is low. It is uneconomic for small factories to start a recovery plant. Roughly speaking, for 110 parts of soap we get 10 parts of glycerine. India can make it from molasses by fermentation; 10 tons of molasses would yield about one ton of glycerine. But unless some new uses of glycerine be found, e.g., manufacture of plastics from glycerine and phthalic acid (glyptal), the prospect is not very bright. India made 3936 tons of it in 1958.

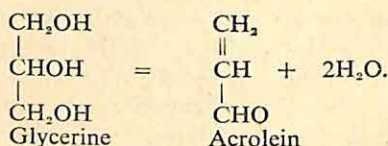
Properties.—Pure glycerine is a colourless, odourless, syrupy liquid, heavier than water (sp. gr. 1·265). It is miscible with water or alcohol in all proportions, but insoluble in ether or chloroform. It is very hygroscopic. Pure glycerine distils unchanged at 290° but decomposes when distilled with water or salts. It is less sweet than glycol. Glycerol crystallises slowly on cooling (m.p. 17°). Its use in medicine is due to its antiseptic properties, and in cosmetics, to its softening action on the skin.

Reactions.—(1) As a trihydric alcohol, glycerine combines with 1, 2 or 3 molecules of monobasic acids giving mono-, di- and tri-esters respectively. Esters of higher fatty acids are oils and fats (p. 112). With sulphuric, nitric or hydrochloric acid, corresponding esters are formed. By far the most notable is glycerine trinitrate (wrongly but commonly called trinitroglycerine), a violent explosive. With HCl gas

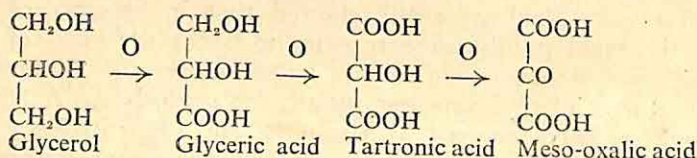
under suitable conditions, mono- and di-esters are formed; but the trichloride is only obtained with phosphorus pentachloride.



(2) When glycerol is heated with dehydrating agents *e.g.*, KHSO_4 , P_2O_5 , etc., acrolein is formed. This serves as a test for glycerine because acrolein has a characteristic, pungent odour.

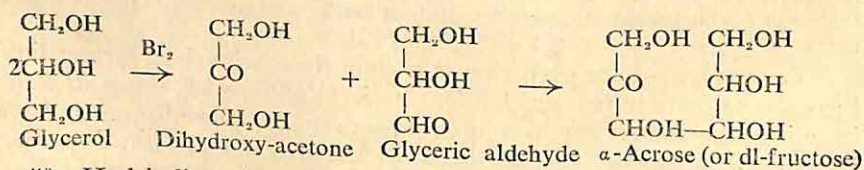


(3) Oxidising agents give various products depending upon conditions:

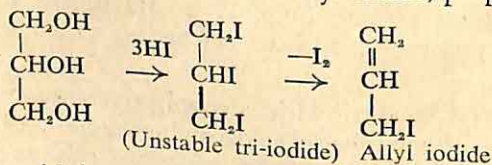


Strong oxidising agents break it down to oxalic acid, carbon dioxide, etc. Thus warm, acidified KMnO_4 solution is decolorised by glycerol, carbon dioxide being evolved.

(4) With bromine and sodium carbonate, dihydroxy-acetone and glyceric aldehyde are formed. These polymerise at 0° to α -acrose, by 'aldol condensation'.

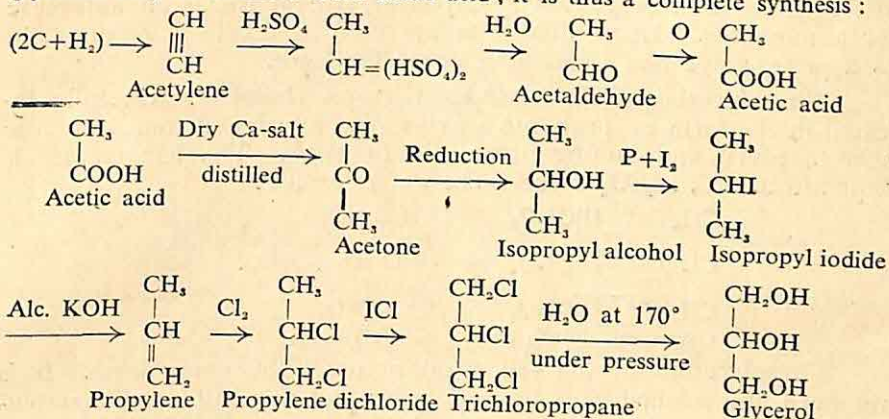


(5) Hydriodic acid reduces it to allyl iodide, propylene, etc.

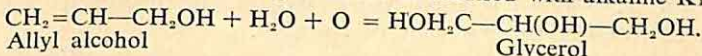


(6) Oxalic acid forms formic acid on heating with glycerol (p. 145). Glycerol yields, on fermentation, *n*-butyl alcohol, butyric acid, ethyl alcohol, etc.

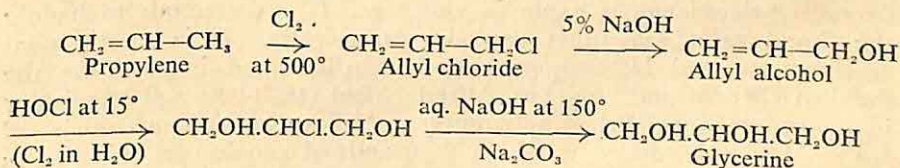
✓ **Synthesis of glycerine.**—Acetic acid may be synthesised from its elements ; glycerine may be obtained from acetic acid ; it is thus a complete synthesis :



Glycerol is formed when allyl alcohol is oxidised with alkaline $KMnO_4$.



Synthetic glycerine.—U.S.A. makes glycerine from propylene which forms nearly 30% of the gases obtained during the cracking of petroleum. Chlorine at high temperature substitutes hydrogen in propylene. The yield is high and the cost low.



Structure of glycerol.—The molecular formula of glycerine is $C_3H_8O_3$. The oxygen occurs as -OH groups because phosphorus pentachloride gives trichloropropane, $CH_2Cl.CHCl.CH_2Cl$. Hence glycerol is $C_3H_5(OH)_3$. That these -OH groups are attached to different carbon atoms follows from (a) the synthesis given above, (b) its stable character, (c) the successive formation of mono-, di- and tri-esters, etc. Hence glycerine is $HOH_2C-CH(OH)-CH_2OH$.

Tests for glycerol.—(i) On heating glycerol with powdered $KHSO_4$, irritating odour of acrolein is noticeable.

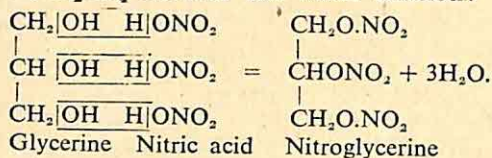
(ii) The pink coloration produced on adding a few drops of phenolphthalein to a dilute solution of borax, disappears on adding glycerol, but reappears on warming.

(iii) It decolorises an acidified dilute solution of $KMnO_4$ on warming with liberation of CO_2 .

Uses.—Glycerine is largely employed in making nitroglycerine, alkyd type plastics, printing and copying inks, transparent soaps, cosmetics, dyestuffs and allyl derivatives. In pharmacy, it is used in cough remedies, lotions, glycerine suppositories, etc.; nitroglycerine is a heart stimulant. For its hygroscopic nature, it is widely used to

keep tobacco moist, in shaving soaps, and also as a softening agent for viscose films (e.g., cellophane). Glycerine, like glycol, is an antifreeze for automobiles. Large quantities are used in textile processing and as a preservative and sweetening agent for foods.

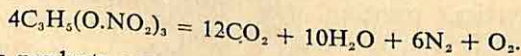
Nitroglycerine, $C_3H_5(O.NO_2)_3$.—Glycerol (1 part) is carefully injected in the form of spray into a well-cooled mixture of conc. sulphuric acid (5 parts) and fuming nitric acid (3 parts). The temperature is kept within 25° , H_2SO_4 absorbs the water formed:



Nitroglycerine, a pale yellow oil, occupies the upper layer. It is removed and washed with ice-cold water and then with a dilute solution of sodium carbonate to remove the last traces of acid which makes it unstable. It is again washed with water and finally dried by filtration through calcined soda or a mat of sponges.

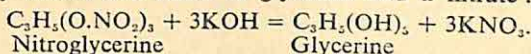
Pure nitroglycerine is a colourless, odourless, heavy oil (sp. gr. 1.6) freezing at 13° . It has a sweet taste and is poisonous; its vapour causes headache and unconsciousness. In minute dose it is a heart stimulant. 1% alcoholic solution reduces high blood pressure. Nitroglycerine ordinarily burns quietly and is harmless, but when rapidly heated or detonated, it explodes violently. It is dangerous to handle the liquid as it sometimes explodes whimsically. It is mostly used as *dynamite* and *blasting gelatine*—both discovered in 1866 by the Swedish chemist and engineer, Alfred Nobel (1833-96), well known for inaugurating Nobel Prizes apparently to 'relieve his human conscience' for making a discovery by which thousands of people can be killed in no time. Nitroglycerine itself was, however, first made in 1847 by an Italian chemist, Sobrero.

Dynamite is usually a mixture of 75% nitroglycerine and 25% kieselguhr—a kind of porous, siliceous earth which absorbs nitroglycerine and forms a soft mass. Sawdust, flour or wood pulp is also used for kieselguhr. Dynamite can be safely handled and transported. It explodes only when detonated and more violently than nitroglycerine itself. Owing to a crack in the container, the nitroglycerine got mixed with the porous earth with which Nobel packed the container. An excellent absorbent for nitroglycerine was thus discovered and dynamite was born. Dynamite is also used for rock-blasting and gold mining. In cold countries, glycerine is mixed with some glycol and nitrated as usual. Dinitroglycol (which thus results) resembles nitroglycerine closely, but has a much lower freezing point. The mixed nitrate (termed polar, arctic, etc.) does not freeze at the ordinary winter temperature. **Blasting gelatine** is a jelly-like mixture of about 7 parts nitrocellulose and 93 parts nitroglycerine. It can be safely manipulated. **Cordite** is the best known nitroglycerine powder used for smokeless rifle cartridges, 5% vaseline and 30% nitroglycerine. It is believed that nitroglycerine decomposes during explosion as



The gaseous products occupy about 10,000 times the volume of the origin* nitroglycerine, hence the explosive violence is so great.

Nitroglycerine should be correctly called glycerol nitrate inasmuch as it is hydrolysed by alkalis like esters to glycerine and a nitrate :



Dynamites now contain ammonium nitrate (55%), sodium nitrate (15%), wood pulp (15%) and a mixture of glycol nitrate and glyceryl nitrate (15%), which serves as the sensitiser for the ammonium nitrate.

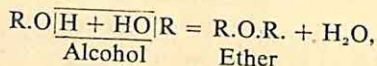
QUESTIONS

1. How is glycerine obtained on a manufacturing scale, and how has its constitution been determined? Mention the various uses of glycerine.—B.Sc., Pass, 1937, Dacca University.
2. What are glycols? How are they prepared? What are the oxidation products of ethylene glycol?
3. What are the actions of (i) phosphorus pentachloride, (ii) dehydrating agents, (iii) nitric acid, and (iv) reducing agents on glycerol?
4. What is glycol? How is it prepared? Discuss fully how its constitution is established.—B.Sc., Pass, 1935, Allahabad University.
5. How is glycerine obtained by fermentation? Discuss the possibilities of its manufacture in India.
6. What is dynamite? How is it manufactured? What are its uses? Is it correct to call it nitro-glycerine? If not, why not?
7. How is glycerine obtained on a large scale? How can it be synthesised? What is the action of (a) HI, (b) KHSO_4 , (c) HNO_3 and (d) NaOBr on glycerine? B.Sc., 1947, Bombay University.
8. How is glycerine obtained on a large scale? How is it synthesised? State its properties and uses. Write what you know about naturally occurring glycerides.—B.Sc., Pass, 1937, Calcutta University.
9. How is glycerine synthesised from its elements? Describe a method for obtaining it on a large scale. How is nitro-glycerine prepared and what are its uses?—B.A., Pass, 1937, Bombay University.
10. Review the evidence bearing on the constitution of glycerol. Discuss the action of HI and oxidising agents on glycerol.—B.Sc., Pass, 1942, Patna University.

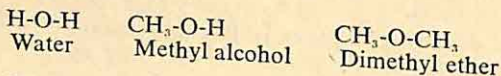
CHAPTER XI

THE ETHERS, $C_nH_{2n+2}O$.

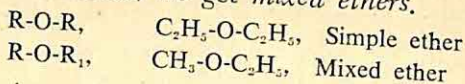
If from two molecules of a monohydric alcohol one molecule of water be eliminated, we get an **ether** :



R being an alkyl group. Ethers may, therefore, be regarded as alkyl oxides, R_2O . R-O- is called *alkoxyl* group ; e.g., CH_3O - is methoxyl group. Ethers are saturated or unsaturated according to the nature of the hydrocarbon radicals. We may also look at them in a different way. Alcohols are alkyl hydroxides, theoretically formed by replacing a hydrogen of water by an alkyl group. Ethers are thus di-alkyl derivatives of water :



If the alkyl groups attached to the oxygen are the same, we have *simple ethers* ; if different, we get *mixed ethers*.



Ethers are isomeric with alcohols but have quite different properties. For example, they are lighter and far more volatile than alcohols, practically insoluble in water and also relatively inert. By far the most important is di-ethyl ether, so much so, that it is simply called ether (*cf.* ethyl alcohol, p. 87). We consider it first.

✓ **Diethyl ether, $\text{C}_2\text{H}_5\text{-O-C}_2\text{H}_5$,** is prepared in the laboratory or factory by heating an *excess* of ethyl alcohol with concentrated sulphuric acid at about 140° . At higher temperature, we get ethylene (p. 57). The method was discovered by Valerius Cordus, a German physician, in 1544.

Preparation.—A 500 c.c. distilling flask is fitted with a separating funnel, a thermometer, and a condenser. 100 c.c. of rectified spirit are taken in the flask and an equal volume of strong sulphuric acid is gradually added with the shaking and cooling. The thermometer and the tap-funnel dip into the liquid ; the tap-funnel contains alcohol. The flask is gradually heated to $140\text{--}145^\circ$ on a sand-bath. The end of the condenser is gradually heated to $140\text{--}145^\circ$ on a sand-bath. The end of the condenser through which ice-cold water is circulated, leads to a receiver, cooled in ice. The side-tube of the receiver is joined with a rubber tubing to the sink so that no ether vapour can reach the flame. The temperature is kept at about 140° ; ether, water and a little alcohol distil over. Fresh alcohol is *slowly* run from the tap-funnel to keep the volume constant. The distillate which contains a little sulphurous acid, is shaken in a separating funnel with dilute caustic soda to remove the acid, then with a strong solution of common salt to dissolve the alcohol. The lower aqueous layer is removed. The ether is dried with fused calcium chloride. The filtered liquid is distilled from a water-bath. Precautions should be taken as before, the vapour

being highly inflammable. The last traces of water or alcohol are removed by allowing the liquid to stand over metallic sodium overnight and re-distillation.

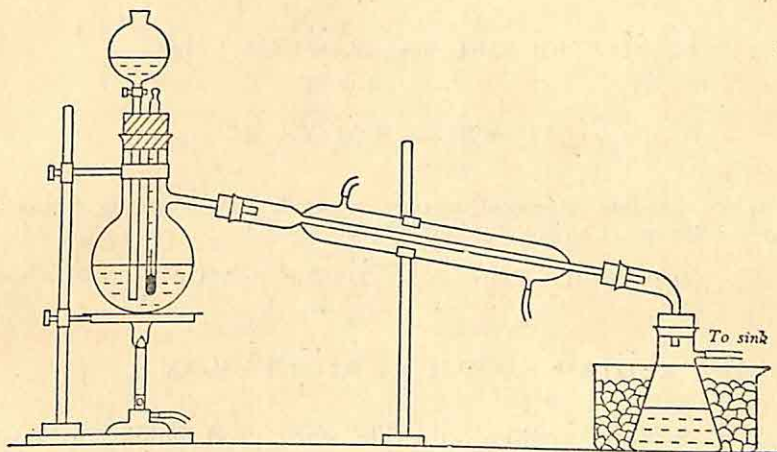
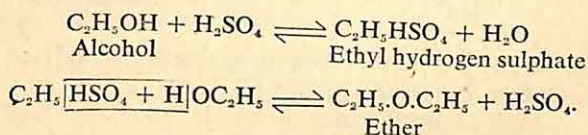
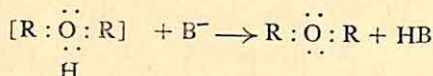
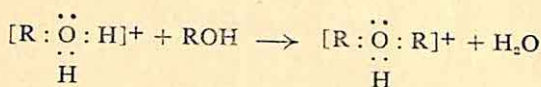
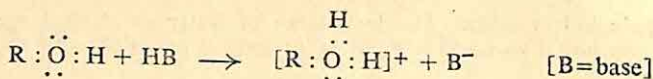


Fig. 28. Preparation of ether.

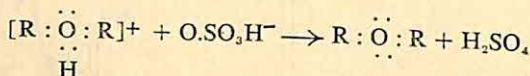
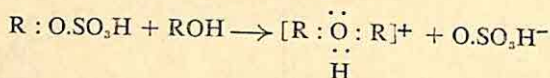


The regenerated sulphuric acid converts more alcohol into ether and the cycle goes on. It is, therefore, known as *continuous etherification process*. But actually the process is seldom continuous due to side-reactions, some sulphuric acid is reduced to sulphur dioxide, etc. After some time, the water formed in the first step dilutes the acid. Nevertheless a small amount of sulphuric acid converts a large quantity of alcohol into ether (one part of H_2SO_4 produces about 200 parts of ether). With benzenesulphonic acid, $\text{C}_6\text{H}_5\text{SO}_3\text{H}$, or syrupy phosphoric acid, which are not reduced, the process is really continuous. With methylated spirit, a less pure product, *methylated ether*, is obtained; it contains some dimethyl and methylethyl ether. By this method, primary and secondary alcohols give ether but tertiary alcohols yield only olefines. Primary butyl alcohol and higher members, however, yield both unsaturated hydrocarbons and ether. The yield of ether is best with primary alcohols which dehydrate to olefines least readily. ✓

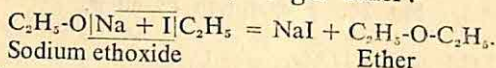
The mechanism of this reaction is not quite clear. The above two-stage theory does not apparently give the complete picture inasmuch as ether can be produced by heating ethyl alcohol with any strong acid such as HCl , HI , H_2SO_3 , picric acid, benzenesulphonic acid, etc. In fact, any electron accepting reagent, e.g., ferric sulphate, zinc chloride, boron fluoride, etc. is effective. Furthermore, HCl catalyses ether formation at 155° at which ethyl chloride and ethyl alcohol do not react to give ether. The formation of ethyl hydrogen sulphate as an intermediate product, when H_2SO_4 is used, is not therefore a necessary step. The conversion of ethanol into ether is thus an acid-catalysed reaction which becomes appreciable above 100° .



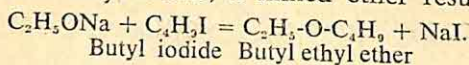
With H_2SO_4 possibly a second reaction proceeds simultaneously, giving ethyl hydrogen sulphate as an intermediate product:



(2) By heating sodium ethoxide with ethyl iodide in alcoholic solution under a reflux condenser, we get ether:

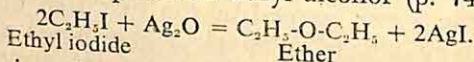


With a different alkyl iodide, a mixed ether results:



This is Williamson's synthesis (1850) of simple and mixed ethers, which almost directly establishes their structure. Alkyl sulphate may replace alkyl iodide in the preparation.

(3) By heating ethyl iodide with dry silver oxide, ether is formed. Moist silver oxide produces ethyl alcohol (p. 74).



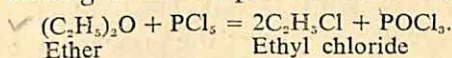
(4) By passing alcohol vapour over alumina or thoria at 240-260°, ether is obtained in nearly 85% yield. At about 360°, however, the main product is ethylene (p. 58).

Ether thus prepared is not related to the hypothetical 'ether' of the physicist, or the so-called 'fifth element' of the Hindus; the name was chosen due to the high volatility of the compound (Greek *aither*, material filling heavenly space).

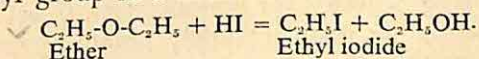
Properties. Ether is a neutral, mobile liquid with a characteristic smell, and a burning taste. It boils at 34.5° and is extremely volatile. Unlike alcohols, ethers cannot associate through hydrogen bonding, which accounts for their low boiling point. It takes fire even when the flame is at some distance. Precautions must be taken while working with it, specially in a hot country like India. The vapour forms (0.720) and is slightly soluble in it (7.5 g in 100 g of water at 20°). The unshared pairs of electrons on oxygen in the ether form hydrogen bond with water, $R_2O \cdots H-O-H$; this accounts for the solubility. It is miscible with alcohol or liquid hydrocarbons in all proportions. Due to rapid evaporation, it produces intense cooling, and so used as a local

anæsthetic. (Taken orally, ether produces intoxication like alcohol but the effect is more transient. Ether is rather unreactive chemically. Metallic sodium or potassium has no action on it as also alkalis.)

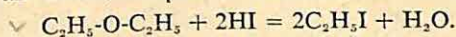
Reactions.—(1) Phosphorus pentachloride does not react with ether at ordinary temperature, but on heating to about 200° , ethyl chloride is formed. The main product is a mixture of chlorinated ethers, chlorine coming from the pentachloride due to dissociation.



(2) When saturated with gaseous hydrogen iodide, ethyl iodide and alcohol are formed at 0° . A larger portion of iodine goes to the smaller alkyl group in a mixed ether.



(3) Strong hydriodic acid (d. 1.7) in excess decomposes ether on heating, mainly to ethyl iodide. By identifying the alkyl halides, the composition of an ether, simple or mixed, can be determined.



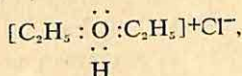
(4) Heated under pressure with dilute sulphuric acid, ether is hydrolysed to alcohol: $\checkmark (C_2H_5)_2O + H_2O = 2C_2H_5OH$.

(5) In sunlight and air, ether slowly forms ether peroxides, e.g., $C_2H_5.O.O.C_2H_5$, or $CH_3.CH.O.CH_2.CH_3$, which are explosive



and highly toxic. That is why explosion sometimes occurs while distilling old ether that has been exposed to air. It should be shaken with ferrous sulphate solution before distillation to destroy any peroxide. Peroxide is also formed when ozone acts on ether. Ether containing even traces of peroxide cannot be used for anæsthesia. It is detected by shaking ether with aqueous potassium iodide solution, the peroxide liberates iodine. Ether for anæsthetic purposes is usually kept in small, coloured glass tubes sealed at both ends. A little alcohol or water prevents peroxide formation.

(6) On shaking with strong mineral acids in the cold, ether forms oxonium salts e.g., diethyl oxonium chloride (m.p. -92°),



a proton of the acid forms a dative bond with a lone pair of electrons of oxygen. Thus ether readily dissolves in strong acids, the solution being an electrolyte. Heated in a sealed tube, HCl splits ether like HI.

(7) Ether reacts like paraffins with Cl_2 or Br_2 in the dark at ordinary temperature to form mono- and di-halogeno-ethers e.g., $CH_3.ClCH.O.CH_2.CH_3$ and $CH_3.CHCl.O.CHCl.CH_3$.

(8) Alkaline $KMnO_4$ oxidises it mainly to acetic acid, and red

phosphorus and HI reduce it to ethane. Passed over alumina at 380° , ether decomposes into ethylene and water.

Formerly ether was supposed to contain sulphur and was called sulphuric ether. Even to-day the name 'ether sulphuric' is used by some manufacturers, presumably on account of its method of preparation.

Constitution of ether.—The molecular formula of ether is $C_4H_{10}O$. Sodium liberates no hydrogen from ether, and phosphorus pentachloride produces two molecules of ethyl chloride but no HCl. This shows the absence of hydroxyl group; the presence of two ethyl radicals follows from Williamson's synthesis of ether from sodium ethoxide and ethyl iodide (p. 120). Hence ether is $C_2H_5-O-C_2H_5$. On treatment with hydriodic acid, ethyl iodide is regenerated.

Uses.—Ether is a solvent for resins, fats, oils, alkaloids and cellulose esters. It readily dissolves many organic compounds and is widely used for extracting them from aqueous solutions. It is a better anæsthetic than chloroform in that it has no depressant action upon the heart, but acts rather slowly. In practice, a mixture of both is used in surgery. When the concentration of ether in the blood exceeds 0.4%, death may be caused by cardiac failure. Mixed with alcohol, it is a petrol-substitute (*Natalite*).

Dimethyl ether, CH_3-O-CH_3 , may be prepared by heating methyl alcohol with sulphuric acid in the same manner as diethyl ether, or by passing the vapour of methanol over alumina at 250° . It is a colourless gas which condenses to a liquid boiling at -23° . Concentrated H_2SO_4 dissolves 600 times its volume, and water 37 times its volume, of the gas at 18° . Dimethyl ether is sometimes employed as a refrigerant. It is isomeric with ethyl alcohol, C_2H_5OH .

Homologues of ether.—Besides dimethyl and di-ethyl ether, there are many others but they are not so important, except *isopropyl ether*, $(CH_3)_2CH.O.CH(CH_3)_2$, obtained as a by-product in making isopropyl alcohol from propylene (p. 96). It is used for extracting acetic and lactic acids from their dilute aqueous solutions and also in high anti-knock fuels for aeroplanes. It is a good solvent for oils, waxes and resins. Homologues of ether may be prepared by methods described under diethyl ether. They closely resemble diethyl ether. Excepting the first two, all other members are liquid—lighter than water and immiscible with it. They are far more volatile than the mother alcohols as they cannot associate by hydrogen bonding. Chemically, as a class, they are inert. By HI or PCl_5 at high temperature, they are decomposed into alkyl halides. Ethers are colourless, neutral and inflammable bodies; the higher members are, however, less volatile and also less inflammable.

The ethers $C_nH_{n+2}O$.

Name	Structure	b.p. $^{\circ}C$	Sp. gr.	m.p. $^{\circ}C$
Dimethyl ether	CH_3-O-CH_3	-23	Gas	-138
Methyl ethyl ether	$CH_3-O-C_2H_5$	8	·647	—
Di-ethyl ether	$C_2H_5-O-C_2H_5$	34.5	·714	-116.5
Di-propyl ether	$C_3H_7-O-C_3H_7$	90.7	·747	-112
Di-isopropyl ether	$C_3H_7-O-C_3H_7$	67.5	·726	-60
Di-n-butyl ether	$C_4H_9-O-C_4H_9$	141	·769	—
Di-isoamyl ether	$C_5H_{11}-O-C_5H_{11}$	172	·783	—

Isomerism of ethers : metamerism.—(i) Ethers are isomeric with alcohols; thus $C_4H_{10}O$ represents diethyl ether, $C_2H_5-O-C_2H_5$, and π -butyl alcohol, $CH_3-CH_2-CH_2-CH_2OH$. Ethers can be distinguished from alcohols with sodium or phosphorus pentachloride (p. 92).

(ii) Ethers may contain alkyl radicals which are isomeric amongst themselves, e.g., dipropyl ether, $CH_3-CH_2-CH_2-O-CH_2-CH_2-CH_3$, and di-isopropyl ether, $(CH_3)_2CH-O-CH(CH_3)_2$.

(iii) Different alkyl radicals may be attached to oxygen of an ether so that the molecular formulæ are the same; e.g., diethyl ether, $C_2H_5-O-C_2H_5$ or $C_4H_{10}O$, and methyl propyl ether, $CH_3-O-C_3H_7$ or $C_4H_{10}O$.

In (ii) and (iii) isomerism, within the series, is due to different alkyl radicals being linked to oxygen. This is called *metamerism*, and the compounds *metameric*. Ketones, esters, amines, etc., also exhibit metamerism.

QUESTIONS

1. What is understood by the continuous etherification process? How can ethyl ether be prepared in a pure form by this method? What are its uses? Enumerate characteristics of ether and state how it can be obtained by other methods.—B.Sc. 1948, Gauhati Uni.

2. What is a mixed ether? How can you identify the nature of a mixed ether?

3. Write down the structures of various ethers having the empirical formula, $C_5H_{12}O$. State how you would prepare any one of the isomerides, and outline method of production of necessary materials.—B.Sc., London, 1931.

4. How is ether manufactured? How would you establish its constitution?

5. Suggest a method for the synthesis of ether from its elements.—B.Sc., Pass 1933, Allahabad University.

6. Ethyl alcohol and methyl ether have the same formula, C_2H_6O . How would you ascertain the structural formula of each? Describe the action of H_2SO_4 on ethyl alcohol.—B.A. & B.Sc. Degree Exam., 1932, Andhra Uni.

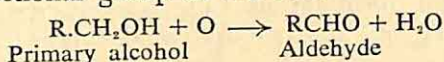
7. How is diethyl ether prepared? How and under what conditions does it react with (a) HI , (b) Br_2 and (c) PCl_3 ? —B.A. Degree Exam., 1941, Madras University.

8. A compound X has 64.68% C, 13.51% H, and 21.62% O; its vapour density is 37. Only strong HI acts on X giving alkyl iodide, having 81.41% I. What is the structure of X?

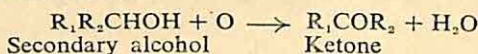
CHAPTER XII

THE ALDEHYDES AND KETONES, $C_nH_{2n}O$.

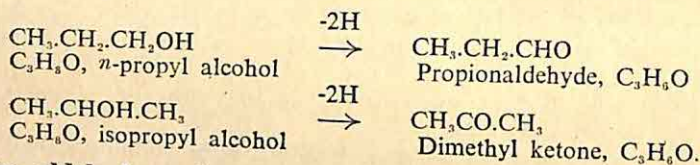
Primary alcohols, on mild oxidation, first part with two atoms of hydrogen and yield **aldehydes** (*alcohol dehydrogenatum*, i.e., alcohol deprived of hydrogen). They contain the monovalent *aldehyde group*, $-CHO$, the functional group of the series.



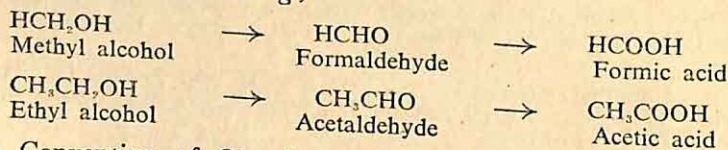
Similarly, secondary alcohols, on oxidation, form **ketones**. Tertiary alcohols cannot be oxidised to aldehydes or ketones without disrupting the carbon chain.



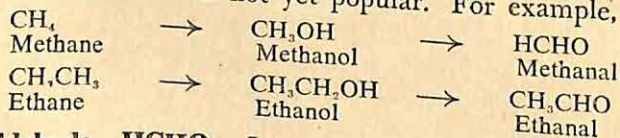
The ketones have the bivalent carbonyl or *ketone group*, $>CO$. This occurs also in aldehydes in which at least one valency of the carbon is satisfied with *hydrogen* (thus forming the $-CHO$ group). In ketones, both are satisfied with alkyl groups. Aldehydes and ketones have the general formulæ $R.CH_2OH$ and $R_1.CO.R_2$ respectively. Due to the common carbonyl group, many of their reactions are similar. Derived from monohydric alcohols (primary or secondary), $C_nH_{2n+2}O$, by the loss of two hydrogen atoms, aldehydes and ketones have the same general formula $C_nH_{2n}O$, and are isomeric.



The aldehydes.—Commonly, aldehydes are named after acids they yield on further oxidation, e.g.,



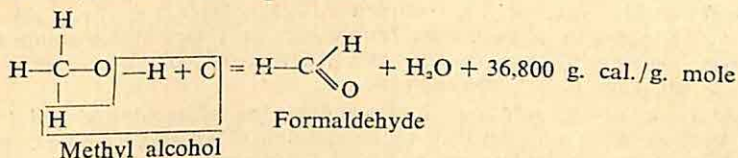
Geneva Convention of Chemists (1892) suggested 'al' for 'e' at the end of paraffins. But this is not yet popular. For example,



Formaldehyde, $HCHO$.—It occurs in traces in the plant cells containing chlorophyll; it is formed during photo-synthesis (p. 131).

Preparation.—Formaldehyde is usually made by passing a mixture of methyl alcohol vapour and air over silver gauze at 550° - 600° , or

iron-promoted molybdenum trioxide at 350-450°. The conversion is above 85% and 90% respectively.



The formaldehyde vapour is absorbed in water and under suitable conditions, 30-40% solution is obtained. Unreacted methanol accompanies the aldehyde and retards its polymerisation.

Take 2-3 drops of methyl alcohol in a hard glass test-tube. Heat strongly in the oxidising flame a small spiral of copper gauze, plunge it quickly into the test-tube and close it immediately with a cork. The black gauze, due to cupric oxide, is reduced to bright metallic copper and on opening the test-tube, pungent odour of formaldehyde is perceptible.

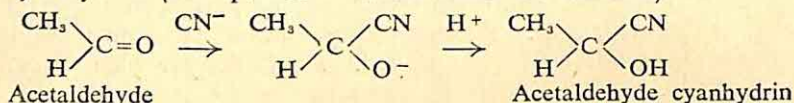
By flameless combustion of methyl alcohol vapour in air in presence of a catalyst, formaldehyde is manufactured. Partial oxidation of methane (natural gas) by air also yields formaldehyde (p. 44) in low yield. This is done in U.S.A. Commercial synthesis of formaldehyde from water gas ($\text{CO} + \text{H}_2$) is not yet a success due to poor yield.

Properties.—Formaldehyde is a pungent gas, which can be condensed to a liquid (b.p. -21°). It is highly soluble in water; a 40% solution is known as *formalin*. In aqueous solution it appears to exist in hydrated form, i.e., as dihydroxymethane or methylene glycol, $\text{H}_2\text{C}(\text{OH})_2$. The aldehyde kills bacteria, probably by coagulating their protein. Formaldehyde is readily oxidised to formic acid, and reduced to methyl alcohol. The general reactions of aldehydes are discussed under acetaldehyde as formaldehyde is somewhat different from others.

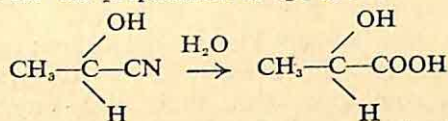
Uses.—Formaldehyde is a common antiseptic and disinfectant as formalin or paraform; it is used for the preservation of biological and anatomical specimens. *Cyclonite*, $(\text{CH}_2)_3\text{N}_3(\text{NO}_2)_3$, which is 1.5 times more powerful an explosive than T.N.T., is made from urotropine (p. 128) and HNO_3 . Formaldehyde is mostly made into plastics e.g., *bakelite*, *galalith*, etc., which are nice substitutes for ivory, amber, bone, etc. It is illegal to preserve milk with formaldehyde. Mixed with lactose, it forms throat lozenges e.g., formamint. It is also used in the manufacture of dyestuffs. Formaldehyde hardens glue or gelatine and makes it insoluble in water, so in the leather industry it replaces tannin. Formaldehyde is also consumed by the plywood industry. U.S.A. made 1.2 billion lb. of formalin in 1955, about 64% entering plastics.

Bakelite is a hard, resinous matter obtained by the catalytic condensation of formaldehyde and phenol. It is a good electric insulator and extensively used for making various domestic articles. The name is after Bakeland of America, the discoverer (1908). **Galalith** is obtained as a horny material by the action of formaldehyde on the casein (protein) of milk. Galalith (*gala* milk, *lithos*

(b) With hydrocyanic acid, aldehydes give *cyanhydrins*. Acetaldehyde gives acetaldehyde cyanhydrin, a colourless liquid (b.p. 103°). The bisulphite compound under (a) also reacts with aqueous KCN and gives the cyanhydrin (*vide* p. 104 for mechanism of reaction).

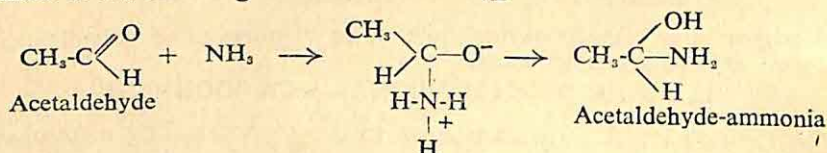


On hydrolysis with acid or alkali, cyanhydrins yield hydroxy-acids and are, therefore, important for the preparation of the latter.



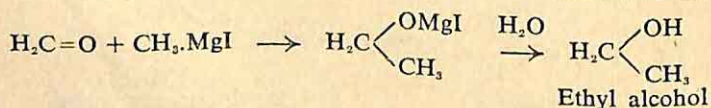
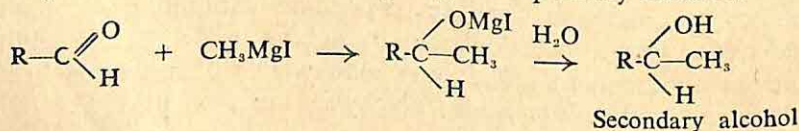
Acetaldehyde cyanhydrin Hydroxy-propionic acid or lactic acid

(c) With *dry ammonia* in the cold, aldehydes in ether solution form *aldehyde-ammonias* which are mostly crystalline, soluble in water but insoluble in ether. We get a trimer, $[\text{CH}_3\text{CH}(\text{OH})\text{NH}_2]_3$, from acetaldehyde. On warming with dilute acids, aldehyde-ammonias reproduce the aldehyde. Aldehydes are thus purified. Nitrogen of NH_3 with its unshared pair of electrons, is nucleophilic; it adds on to the carbonyl carbon as does CN^- , its hydrogen is now less firmly attached to N, one H gets attached to oxygen.

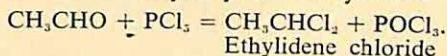


Formaldehyde gives no aldehyde-ammonia but forms a white, crystalline, polycyclic compound, hexamethylene tetramine, *hexamine*, or urotropine, $(\text{CH}_2)_6\text{N}_4$, and water. It is used in cases of urinary troubles. In normal human urine which is acidic, formaldehyde is slowly set free from urotropine, and hence the antiseptic action. If the urine is not acid, hexamine is administered with NaH_2PO_4 which makes it acid. Hexamine is prescribed in gout and rheumatism; it is an accelerator for the vulcanization of rubber. *Cyclonite*, a high explosive, is made from hexamine by nitration.

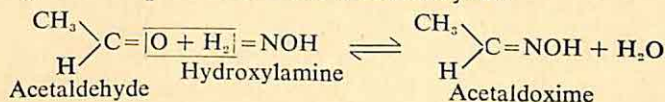
(d) Aldehydes form additive compounds also with Grignard reagent, CH_3MgI , which ultimately yield secondary alcohols on hydrolysis. Naturally, formaldehyde gives a primary alcohol:



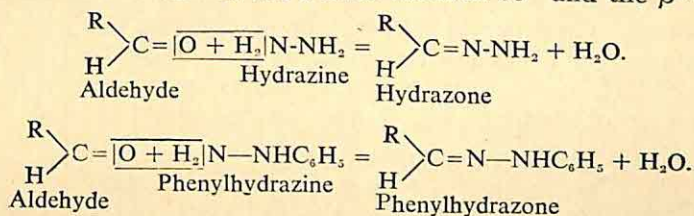
(iv) Aldehydes with PCl_5 yield dichloroparaffins. No hydrochloric acid is liberated. Acetaldehyde yields ethylidene chloride (p. 77).



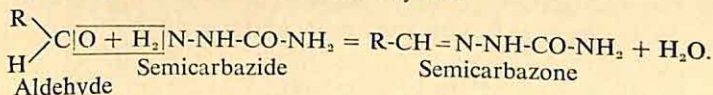
(v) Hydroxylamine in aqueous solution replaces the aldehydic oxygen by the oxime group, $>\text{NOH}$, forming *aldoximes*; oximes are hydrolysed by acids to free aldehydes. Acetaldoxime, a colourless solid (m.p. 47°), is thus produced from acetaldehyde:



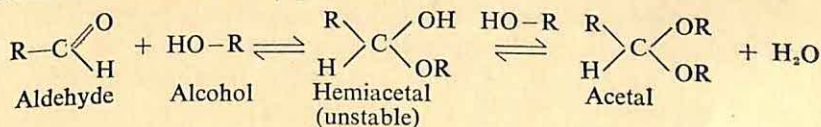
(vi) Hydrazine or phenylhydrazine, in dilute acetic acid solution, forms with aldehydes crystalline *hydrazones* or *phenylhydrazones*. Acetaldehyde gives acetaldehyde phenylhydrazone, $\text{CH}_3\text{CH}=\text{N}\cdot\text{NHC}_6\text{H}_5$, which exists in two forms; the α -form melts at 98° and the β - at 57° .



(vii) Semicarbazide reacts similarly with aldehydes to form *semicarbazones*. Acetaldehyde yields acetaldehyde semicarbazone, $\text{CH}_3\text{CH}:\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, a colourless solid (m.p. 162°). Aldoximes, phenylhydrazones, semicarbazones, etc., being crystalline solids with sharp m.p., help identification of aldehydes.

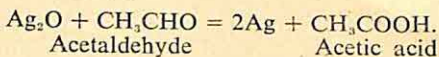


(viii) Aldehydes and alcohols, on heating in presence of dry HCl gas or fused calcium chloride, form *acetals* and water. Acetaldehyde and ethyl alcohol yield *acetal*, a pleasant-smelling, colourless, solvent (b.p. 104°), soluble in water. It is used in veterinary medicine. Acetals are hydrolysed by acids but not by alkalis. Formaldehyde and methanol at 100° give methylal, $\text{HCH}(\text{OCH}_3)_2$, a liquid (b.p. 42°), soluble in water. It is a soporific. When primary alcohols are oxidised with potassium dichromate and dilute sulphuric acid to aldehydes, acetals are obtained as by-products.

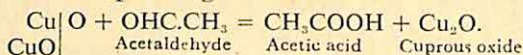


Acetal and methylal are usually obtained from the corresponding alcohols by partial oxidation with MnO_2 and H_2SO_4 . The aldehyde, first formed, condenses with the excess of alcohol to give the acetal.

(ix) Aldehydes are strong reducing agents; they are readily oxidised by alkaline silver or cupric salts to carboxylic acids. (a) Ammoniacal solution of silver nitrate and acetaldehyde give on warming metallic silver and acetic acid.

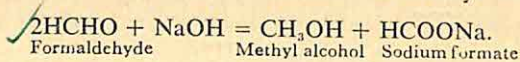


(b) An alkaline solution of cupric salt (e.g., Fehling's solution) is reduced to red cuprous oxide on warming with an aldehyde which is oxidised to the corresponding acid.



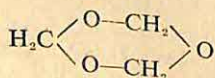
(x) Aldehydes restore the colour of Schiff's reagent (fuchsine or magenta solution decolorised with sulphur dioxide) in the cold. It is a delicate test but not characteristic of aldehydes alone; some ketones and oxidising agents behave likewise.

(xi) Many aldehydes deposit a yellow, resinous solid on heating with dilute caustic alkalis. Formaldehyde is an exception; in presence of conc. NaOH in the cold, one molecule is oxidised to formic acid at the expense of another which is reduced to methyl alcohol.

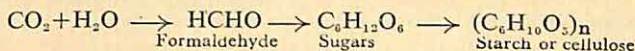


This is Cannizzaro reaction given by aldehydes having no hydrogen in the α -position e.g., $\text{R}_3\text{C} \cdot \text{CHO}$. In presence of aluminium ethoxide, however, acetaldehyde forms ethyl acetate, $\text{CH}_3\text{COO} \cdot \text{CH}_2\text{CH}_3$ (p. 132). S. Cannizzaro (1826-1910), professor of chemistry in Rome, discovered the reaction in 1853.

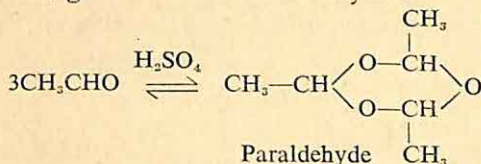
(xii) **Polymerisation of aldehydes.**—The aldehydes have a general tendency to polymerise. The polymers of formaldehyde are the most important (cf., polymerisation of acetylene, p. 68). Liquid formaldehyde polymerises even at its boiling point (-21°) and at higher temperatures, with explosive violence. On evaporating an aqueous solution of formaldehyde (and also at ordinary temperatures), *paraformaldehyde* or *paraform*, $(\text{CH}_2\text{O})_x$, is obtained. It is a white powder (m.p. 140° - 160°) of unknown molecular weight; it reduces Fehling's solution, and is moderately soluble in water. On heating, formaldehyde gas is produced, which condenses back to paraform. It is a fumigant for disinfection. A second, crystalline polymer (m.p. 62°), *meta-formaldehyde*, *trioxymethylene* or *trioxan*, $(\text{CH}_2\text{O})_3$, is formed in presence of a little conc. H_2SO_4 or when paraform is heated with dilute H_2SO_4 . It is soluble in water and smells like chloroform. It sublimes readily and is soluble in water, alcohol and ether. Like paraform, it yields formaldehyde gas when heated. It does not reduce Fehling's solution and has the constitution



In presence of lime-water or other weak alkalis, formaldehyde polymerises at ordinary temperature forming a mixture of sugars, called formose, some of which have the formula, $C_6H_{12}O_6$. Emil Fischer isolated α -acrose therefrom. The process is important as it indicates how, in nature, sugars are possibly produced by plants from carbon dioxide and water which have been shown to form formaldehyde under suitable conditions. Traces of formaldehyde have been detected in plants. Presumably, plants synthesise formaldehyde first (in presence of sunlight and chlorophyll); this polymerises into simple sugars which, by further polymerisation and dehydration, form starch, cellulose, etc.

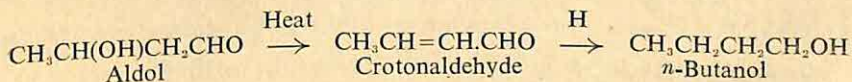
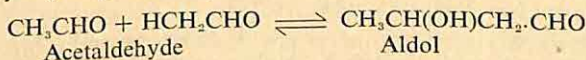


On adding a little conc. H_2SO_4 to anhydrous acetaldehyde, *paraldehyde*, $(CH_3CHO)_3$, is formed with evolution of heat. It is a colourless liquid (b.p. 124°) with a pleasant odour but unpleasant taste, sparingly soluble in water. It is an effective hypnotic. Paraldehyde, a cyclic trimer, gives no test for aldehydes:



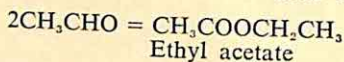
Equilibrium is reached at 95% conversion of acetaldehyde. On distilling paraldehyde with dilute H_2SO_4 , acetaldehyde is obtained back. Acetaldehyde also polymerises to paraldehyde slowly on standing. A second polymer, *metaldehyde*, is obtained when acetaldehyde is treated with a little SO_2 gas, HCl gas, or $CaCl_2$ at low temperature. It is crystalline and insoluble in water. It does not behave as an aldehyde, and is believed to be a cyclic tetramer. Metaldehyde sublimes unchanged at 112° but on distilling with dilute H_2SO_4 , yields acetaldehyde back. Metaldehyde is used as a fuel ('meta fuel').

If acetaldehyde is treated with $ZnCl_2$, dilute alkali, or acid at ordinary temperature, a third polymer, *aldol* or β -hydroxybutyric aldehyde, is obtained, which, unlike the other two, does not reproduce the aldehyde easily. Similar processes are known as *aldol condensation*. Aldol is dehydrated at 180° mainly to crotonaldehyde which is commercially hydrogenated to *n*-butanol (p. 97).

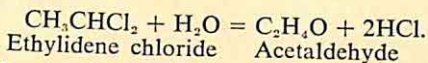


Having both aldehydic and hydroxyl group, aldol responds to the tests for aldehyde and alcohol, whence the name. It is an odourless, syrupy liquid (b.p. 83° at 20 mm.), soluble in water. Aldol is used in making some perfumes and rubber vulcanizers. Two aldehydes or ketones (same or different) or a ketone and an aldehyde may take part in aldol condensation in which only the α -hydrogen atoms are involved.

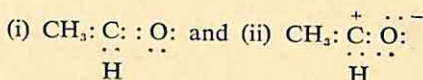
Acetaldehyde forms, in 95% yield, ethyl acetate by *dismutation* when treated with aluminium ethoxide at room temperature. This is **Tishchenko reaction** which is similar to Cannizzaro reaction. The product here is an ester and not a mixture of an alcohol and an acid as in the latter reaction.



Structure of acetaldehyde.—The molecular formula of acetaldehyde is $\text{C}_2\text{H}_4\text{O}$. (i) It has no $-\text{OH}$ group as it liberates no hydrogen with sodium, and no HCl with PCl_5 . (ii) With PCl_5 , acetaldehyde forms ethylidene chloride, CH_3CHCl_2 , i.e., two chlorine atoms replace the oxygen (cf. ethers, p. 121). (iii) Ethylidene chloride, on hydrolysis, forms acetaldehyde; the carbon atoms in acetaldehyde are, therefore, directly linked.



Hence one $-\text{CH}_2-$ group occurs in acetaldehyde which, therefore, has the structure, $\text{CH}_3-\text{C} \begin{smallmatrix} \text{O} \\ \parallel \\ \text{H} \end{smallmatrix}$. Two electronic structures are possible viz.



The true structure is an intermediate between the two, a resonance hybrid (p. 106). The keto group has sufficient polar character. Nucleophilic reagents activate an aldehyde group which reacts in form (ii).

Uses.—Acetaldehyde which is less important than formaldehyde, has some use in dye manufacture. It is chiefly made into alcohol, acetic acid and butanol, and employed as an antiseptic inhalant in nasal catarrh. Acetaldehyde-ammonia is a rubber accelerator.

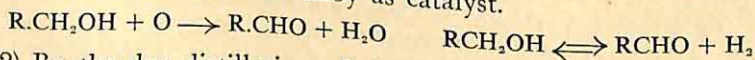
Tests for acetaldehyde.—(i) A blue colour is produced with sodium nitroprusside and piperidine and a cherry-red coloration with sodium nitroprusside and dilute caustic soda solution in excess.

(ii) It reduces ammoniacal silver nitrate or Fehling's solution, restores the colour of Schiff's reagent, and gives crystals of semicarbazone (m.p. 162°) or *p*-nitro-phenylhydrazone (m.p. 128°). Acetaldehyde also gives the iodoform reaction.

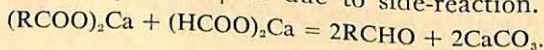
Reactions in which formaldehyde differs from other aldehydes :

- (i) With dry ammonia, formaldehyde gives no aldehyde-ammonia but forms urotropine (p. 128).
- (ii) With caustic soda, formaldehyde produces no resin, but forms formic acid and methyl alcohol simultaneously (p. 130).
- (iii) With phenol, it gives products like bakelite by repeated condensation.

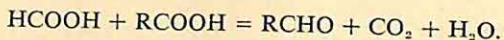
General methods of preparation.—(1) By the oxidation of primary alcohols with $\text{K}_2\text{Cr}_2\text{O}_7$ and dilute H_2SO_4 , or by passing air and the alcohol vapour over silver at about 250° . By dehydrogenation of the alcohol at 325° using Cu-Zn alloy as catalyst.



(2) By the dry distillation of the calcium salt of a fatty acid with calcium formate; the yield is poor due to side-reaction.



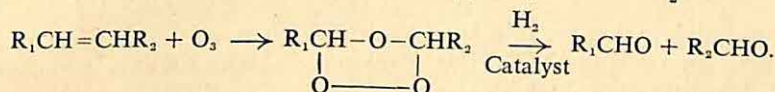
(3) By passing the vapour of formic acid and another fatty acid over manganous oxide, MnO , at 300° .



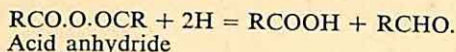
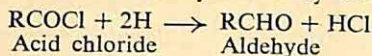
(4) By the hydrolysis of unsymmetrical dihalides of the paraffins having the halogens at the end carbon:



(5) By ozonolysis of olefines of the type $\text{R}_1\text{CH}=\text{CHR}_2$.



(6) From acid chlorides or anhydrides by catalytic reduction:



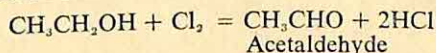
Hydrogen is passed into the acid chloride dissolved in boiling toluene or xylene containing palladium dispersed on the surface of finely divided barium sulphate as catalyst. Barium poisons the catalyst partially so that the aldehyde is not reduced to alcohol.

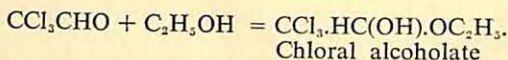
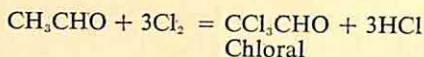
General properties.—The lower members of the series are colourless, volatile, neutral liquids (formaldehyde—and also acetaldehyde in a hot climate—is a gas at ordinary temperature). Their volatility decreases, and density, b.p., etc., increase with rise in mol. wt. The boiling points of aldehydes (and also of ketones) are much lower than those of parent alcohols; this is due to the fact that they having no hydroxyl group, cannot form hydrogen bridges and associate. The higher members are not of much importance; a few are used in perfumery. Their chemical properties are exhibited by the reactions of acetaldehyde.

The aldehydes, $\text{C}_n\text{H}_{2n}\text{O}$.

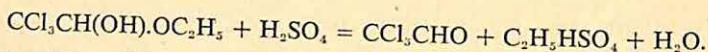
Name	Formula	b.p. °C.	sp. gr.
Formaldehyde	HCHO	-21	'815 at -20°
Acetaldehyde	CH_3CHO	20·8	'79
Propionaldehyde	$\text{C}_2\text{H}_5\text{CHO}$	49	'807
<i>n</i> -Butyraldehyde	$\text{C}_3\text{H}_7\text{CHO}$	73	'817
<i>n</i> -Valeraldehyde	$\text{C}_4\text{H}_9\text{CHO}$	102	'819
<i>n</i> -Caproicaldehyde	$\text{C}_5\text{H}_{11}\text{CHO}$	128	'834

Chloral, trichloro-acetaldehyde, CCl_3CHO , is prepared by saturating cold alcohol with dry chlorine at low temperature and then at 80° – 90° for 5–6 days. Chlorine first oxidises alcohol to acetaldehyde which it next chlorinates to chloral. Chloral and ethyl alcohol react to yield chloral alcoholate.

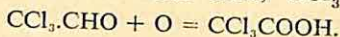




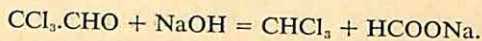
Solid chloral alcoholate is separated and distilled with strong H_2SO_4 to obtain crude chloral. This is neutralised with calcium carbonate and redistilled.



Chloral is a heavy, oily liquid with pungent odour, boiling at 97° . It is used in making D.D.T. It gives most of the aldehydic reactions. HNO_3 oxidises it to trichloro-acetic acid, CCl_3COOH .



Warm NaOH solution gives chloroform (p. 78) but no resinous product.

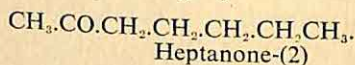
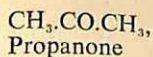


In presence of traces of acids, it polymerises to a white, amorphous powder, called meta-chloral. Chloral combines readily with water with evolution of heat, forming crystalline chloral hydrate, $\text{CCl}_3\text{CHO.H}_2\text{O}$, or $\text{CCl}_3\text{CH(OH)}_2$, which only partially decomposes even at 100° . This is rather unusual as two -OH groups are attached to the same carbon atom. Its stability is due to the inductive effect of chlorine atoms which pull electrons from the C of carbonyl group (cf. trichloroacetic acid) making it relatively positive so that -OH⁻ ions remain attached to this carbon.

Chloral hydrate is crystalline (m.p. 57°) and soluble in water; it has a characteristic smell and a sharp taste. It does not polymerise or respond to Schiff's test, but reduces ammoniacal silver nitrate. Chloral hydrate, once an important hypnotic and a stimulant, has largely been replaced by better soporifics.

Bromal, CBr_3CHO , and bromal hydrate, $\text{CBr}_3\text{CHO.H}_2\text{O}$, as also iodal, Cl_3CHO , and its hydrate are known; they are prepared in a similar manner.

The ketones, $\text{C}_n\text{H}_{2n}\text{O}$.—As already stated, secondary alcohols, on oxidation, yield ketones having two alkyl radicals linked to the -CO- group. They may be the same or different, giving *simple* or *mixed* ketones (cf., simple and mixed ethers, p. 118) respectively. Thus dimethyl ketone, $\text{CH}_3\text{CO.CH}_3$, is a simple, and ethyl methyl ketone, $\text{CH}_3\text{CO.C}_2\text{H}_5$, is a mixed ketone. Ketones are commonly named after the alkyl groups attached to the carbonyl. The Geneva nomenclature adds '—one' after the name of the corresponding hydrocarbon; e.g.,



[(2) means that the second carbon atom from one end is ketonic]

Acetone, dimethyl ketone, $\text{CH}_3\text{CO.CH}_3$, the simplest and the most important, occurs in traces in the blood and normal urine, but often in larger amounts in the urine of diabetic patients. It may be obtained by fractionating the aqueous distillate of wood distillation (p. 85) which contains about 0.5%. A constant-boiling mixture

(b.p. 55.9°), with 90% acetone and 10% methanol, makes purification difficult.

Preparation.—(1) Acetone is prepared in the laboratory by the dry distillation of fused calcium acetate.

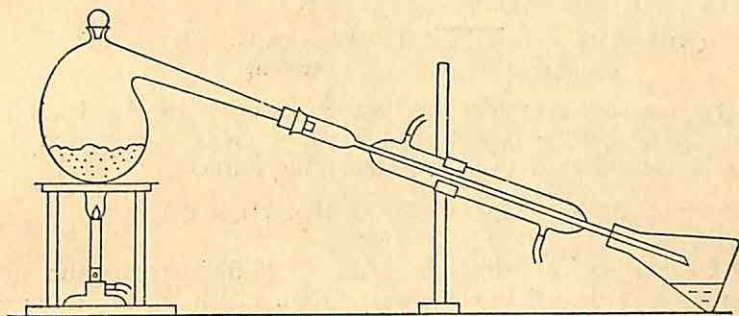
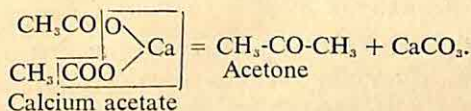


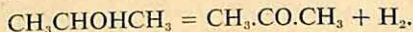
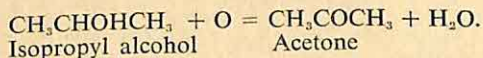
Fig. 29. Preparation of acetone.



About 50 g. of powdered fused calcium acetate is taken in a retort connected to a Liebig's condenser and a receiver. The retort is slowly heated on a wire-gauze; acetone distils over. The distillate is shaken with a saturated solution of sodium bisulphite. The crystalline acetone sodium-bisulphite compound formed, is filtered off and distilled with a saturated solution of sodium carbonate. The distillate containing acetone and water is dehydrated with fused calcium chloride and re-distilled to obtain the pure ketone. The industrial method uses 'acetate of lime' from wood distillation.

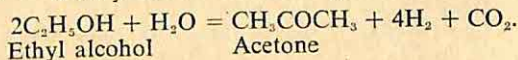
This is a general method for preparing higher ketones. By distilling calcium acetate with the calcium salt of other fatty acids (except formic acid), mixed ketones, in addition to simple ketones, are obtained.

(2) Oxidation of isopropyl alcohol with potassium dichromate and sulphuric acid yields acetone (*cf.* formation of aldehydes from primary alcohols). Industrially, however, the alcohol is dehydrogenated to acetone by passing its vapour over finely divided copper at 300° , or over zinc oxide mounted on pumice at 380° . Hydrogen is a valuable bye-product.

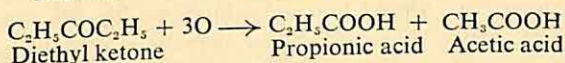


U.S.A. makes isopropyl alcohol from propylene, a bye-product of the petroleum industry (p. 96).

(3) Great Britain makes it by reacting ethyl alcohol with superheated steam (1:4) in presence of a catalyst containing iron and calcium at 470° . The yield is about 80%.

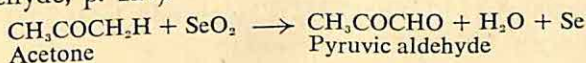


Reactions.—(1) *Oxidation*: Ketones are much less readily oxidised than aldehydes; they are not, therefore, reducing agents. They do not reduce Fehling's solution or ammoniacal silver nitrate. Strong oxidising agents *e.g.*, chromic acid, yield acids having a *smaller* number of carbon atoms. Acetone forms acetic acid, diethyl ketone gives propionic acid, and so on.

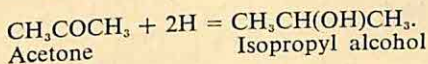


On oxidation, a ketone breaks on either side of the $-\text{CO}-$ group, and may give four acids; the longer alkyl group, however, gets oxidised more quickly. By identifying them, the structure of a ketone, simple or mixed, may be ascertained.

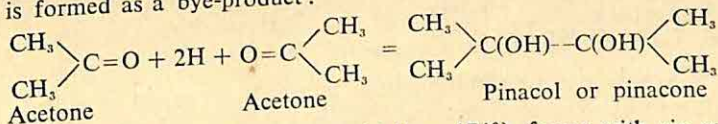
(2) Selenium dioxide, SeO_2 , oxidises acetone to pyruvic aldehyde (*cf.*, acetaldehyde, p. 127).



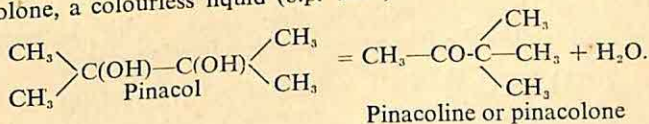
(3) *Reduction*: Ketones, on reduction with nascent hydrogen (*e.g.*, from sodium amalgam and water), yield, in part, the corresponding secondary alcohols. Acetone thus produces isopropyl alcohol. Acetone vapour and hydrogen, passed over freshly reduced nickel at 120° , yield only the alcohol. The method is followed industrially.



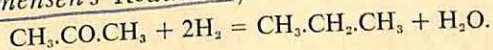
During reduction in aqueous solution with a metal, pinacol, a dihydric alcohol, is formed as a bye-product:



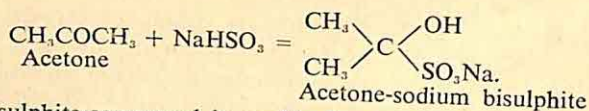
Anhydrous pinacol, a colourless liquid (b.p. 174°), forms with six mols. of water large, plate-like crystals (m.p. 45°) (Greek *pinako* table). On heating with dilute H_2SO_4 or HCl , it loses water and by an intra-molecular change yields pinacolone, a colourless liquid (b.p. 106°).



Refluxed with amalgamated zinc and dilute HCl , acetone gives propane (*Clemmensen's Reduction*).

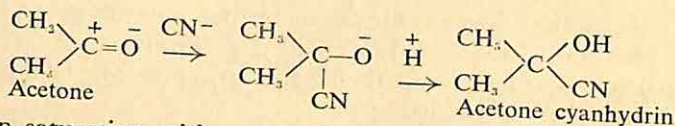


(4) *Additive reactions*: (a) Acetone forms bisulphite compound with *saturated* sodium bisulphite, but much more slowly than acetaldehyde. The product gives back acetone on boiling with sodium carbonate solution. Crude acetone can thus be purified.

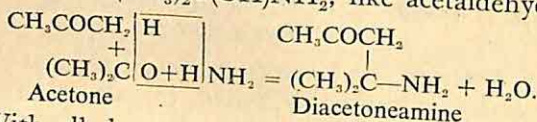


The bisulphite-compound is readily formed if one of the radicals is methyl (i.e., $\text{CH}_3\text{CO-R}$); otherwise, the reaction is extremely slow. Ketones that do not form bisulphite compounds, do not also yield cyanhydrins with HCN .

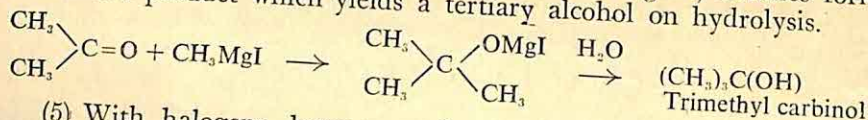
(b) With hydrocyanic acid, ketones yield cyanhydrins but less readily than aldehydes. With higher ketones no reaction occurs. Acetone gives acetone cyanhydrin, a colourless liquid. The bisulphite compound in (a) and aqueous KCN yield the cyanhydrin more conveniently.



(c) On saturation with ammonia, acetone slowly forms a condensation product at room temperature. At -65° , however, acetone gives acetone-ammonia, $(\text{CH}_3)_2\text{C}(\text{OH})\text{NH}_2$, like acetaldehyde.

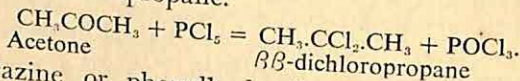


(d) With alkyl magnesium halide (Grignard reagent) ketones form an additive product which yields a tertiary alcohol on hydrolysis.

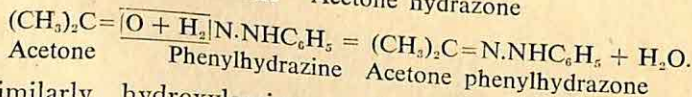
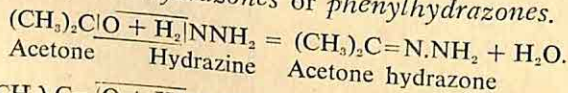


(5) With halogens, ketones produce halogen-substituted products. Acetone with chlorine gives finally hexachloro-acetone, $\text{CCl}_3\cdot\text{CO}\cdot\text{CCl}_3$; trichloro-acetone, $\text{CCl}_3\text{COCH}_3$, is an intermediate product. Chloro-acetone, $\text{CH}_3\text{COCH}_2\text{Cl}$, is a powerful lachrymator.

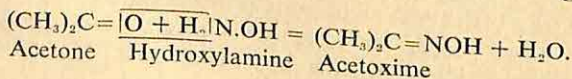
(6) Phosphorus pentachloride acts on ketones in general, producing dichloro-derivatives, but no HCl is evolved. Acetone is thus converted into $\beta\beta$ -dichloropropane.



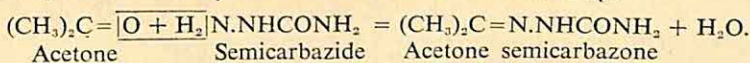
(7) Hydrazine or phenylhydrazine reacts with ketones, as with aldehydes, and yields *hydrazones* or *phenylhydrazones*.



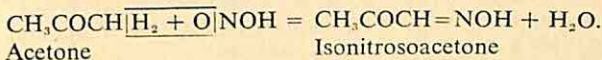
(8) Similarly, hydroxylamine produces *ketoxyimes* with ketones (cf., aldehydes). Acetoxime gives acetone on distilling with dilute H_2SO_4 .



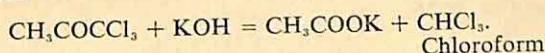
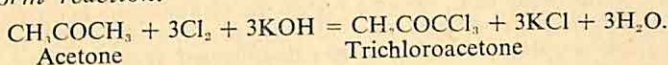
(9) Semicarbazide, like hydrazine, gives *semicarbazones* with ketones; these are crystalline and have definite m.p.



(10) With nitrous acid, acetone forms an isonitroso-derivative:



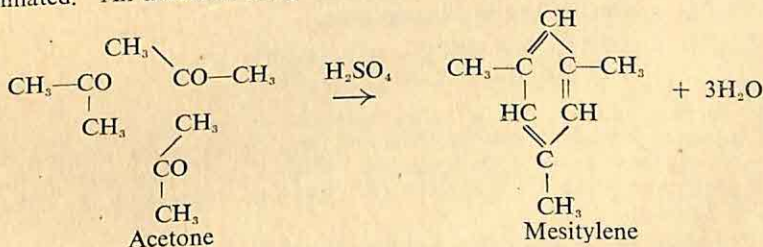
(11) With bleaching powder or chlorine in alkaline solution, acetone yields chloroform (p. 78). Similarly, we get bromoform or iodoform with bromine or iodine in alkaline solution. This is known as *haloform reaction*.



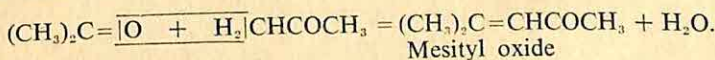
Condensation reactions.—Sometimes two or more molecules, same or different, unite to form a more complex molecule with a new linkage between carbon atoms. These are known as condensation reactions, and the products as condensation products; usually but not invariably, there is elimination of water, alcohol, HCl, etc.. The term is rather elastic and difficult to define precisely. A new carbon-nitrogen linkage is also included in such reactions. Formation of aldol from aldehyde (p. 131), pinacol from acetone (p. 137), are instances.

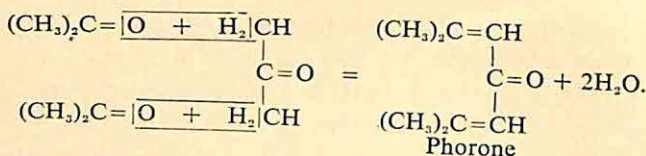
Polymerisation, unlike condensation, is a self-addition reaction which is *repeated* until a compound of very high mol. wt. results.

(12) **Condensation of acetone.**—Unlike aldehydes, ketones have little tendency to polymerise, but they form condensation products under suitable conditions with elimination of water. (i) Acetone forms trimethylbenzene or mesitylene when distilled with twice its weight of 80% H_2SO_4 . Three molecules of acetone take part in the reaction, an equal number of water molecules being eliminated. An aromatic compound is obtained from an aliphatic.

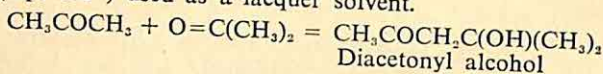


(ii) When acetone is kept for some time saturated with dry HCl gas, two unsaturated ketones, mesityl oxide (an oil, b.p. 130°) and phorone (a yellow solid, m.p. 28°) are formed; these may be separated by fractional distillation. Both give acetone with hot, dilute H_2SO_4 . The former is a misnomer as it is an unsaturated ketone and not an oxide; the latter is so called because it is a ketone with a camphor-like odour (*camphor* + acetone).

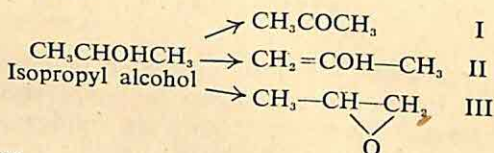




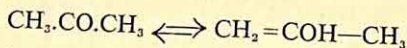
(iii) Acetone slowly undergoes 'aldol' condensation at 0° in presence of strong NaOH solution or solid baryta, $\text{Ba}(\text{OH})_2$, giving diacetyl alcohol, an oily liquid (b.p. 168°) used as a lacquer solvent.



Structure of acetone.—(i) The molecular formula for acetone is $\text{C}_3\text{H}_6\text{O}$. (ii) When isopropyl alcohol is oxidised, it loses two atoms of hydrogen and gives acetone. (iii) With PCl_5 , acetone forms $\beta\beta$ -dichloropropane, $\text{CH}_3\text{CCl}_2\text{CH}_3$, but no HCl, showing the absence of $-\text{OH}$ group. (iv) Thus the hydrogen of the $-\text{OH}$ group in isopropyl alcohol has disappeared during oxidation. This is possible in three ways:

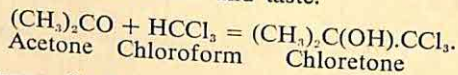


(v) II and III cannot explain the formation of $\beta\beta$ -dichloropropane from acetone and PCl_5 , and of hydrazone, semi-carbazone, diacetyl alcohol, etc. as does I. Hence acetone is CH_3COCH_3 . Since perfectly dry acetone slowly liberates hydrogen with sodium, acetone is believed to exist in forms I and II in equilibrium.



Uses.—Acetone is a solvent for nitro-cellulose, cellulose acetate and acetylene. It is employed for making *sulphonal*—a soporific, *irone*—an artificial scent, *cordite*, a smokeless powder, *Plexiglas*, a methyl methacrylate plastic (unbreakable glass in aircraft) and ketene. Chloroform and iodoform are made from acetone (pp. 78-79).

Chloretone, a hypnotic and a sedative, specially in motion sickness, is made by reacting acetone with chloroform and solid KOH (cf., reaction 4 (b) on p. 138). It has a camphor-like odour and taste.



Tests for acetone.—(i) To a dilute solution of acetone, add a freshly prepared solution of sodium nitroprusside and then caustic soda solution drop by drop—an orange-red colour is developed, which turns yellow after a while. Traces of acetone in urine are thus detected. But any ketone with the CH_3CO -group gives this test.

(ii) Iodine in potassium iodide solution is added to ammonia until slightly brown. Acetone is then added and warmed. On standing for a few minutes, crystals of iodoform separate. But any ketone containing the CH_3CO -group gives iodoform. Ethyl alcohol gives iodoform with iodine and caustic soda but not with iodine and ammonia.

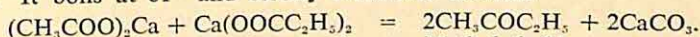
(iii) Acetone restores the colour of Schiff's reagent very slowly.

(iv) The semicarbazone of acetone melts at 187° .

The pre-war consumption of acetone in India was only 25 tons per year chiefly for storing acetylene. About 700 tons are now made annually from

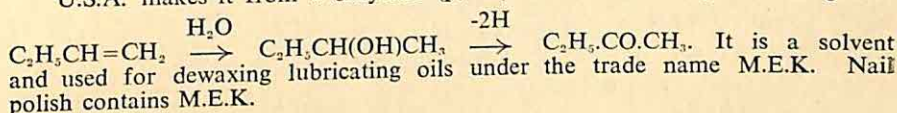
alcohol. In 1955 U.S.A. made 539 million lb. of acetone, 81% of which came from isopropyl alcohol; the cost per lb. was 50 cents in 1918 but only 6 cents in 1955.

Methylethyl ketone, $C_2H_5.CO.CH_3$, is a bye-product in the manufacture of acetic acid from *n*-butane (p. 149) or acetone from wood-spirit, and may be obtained by the dry distillation of a mixture of calcium acetate and calcium propionate. It boils at 81° and closely resembles acetone.



Calcium acetate Calcium propionate Methylethyl ketone

U.S.A. makes it from *n*-butylene (p. 61) of the cracked petroleum gases :



The ketones, $C_nH_{2n}O$.

Name	Formula	b.p. $^\circ C$	Sp. gr.
Acetone, dimethyl ketone ...	CH_3COCH_3	56.5	.792
Methylethyl ketone ...	$CH_3COC_2H_5$	81	.805
Diethyl ketone ...	$C_2H_5COC_2H_5$	101	.814
Dipropyl ketone ...	$C_3H_7COC_3H_7$	144	.821
Di-isopropyl ketone ...	$C_3H_7COC_3H_7$	124	.806
Di-amyl ketone ...	$C_5H_{11}COC_5H_{11}$	227	.826

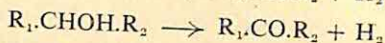
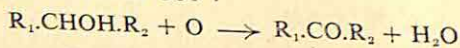
Common reactions of aldehydes and ketones : Both produce

- Cyanhydrins with hydrocyanic acid.
- Bisulphite compounds with sodium bisulphite.
- Oximes with hydroxylamine.
- Hydrazones and phenylhydrazones with hydrazine and phenylhydrazine respectively.
- Additive compounds with Grignard reagent.
- Dichloro-derivatives with phosphorus pentachloride.

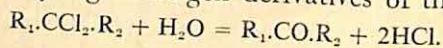
Differences in the behaviour of aldehydes and ketones

	Aldehydes	Ketones
(i) On reduction	Give primary alcohols	Give secondary alcohols
(ii) On oxidation	Form acids with the same number of C-atoms	Form acids with a fewer number of C-atoms
(iii) With ammonia	Give aldehyde-ammonias	Give ketone-amines
(iv) With caustic alkali	Form resins (except form-aldehyde)	Form resins
(v) Polymerisation	Form polymers	Form no polymers
(vi) Condensation	Yield condensation products of the type of acetals and aldols	Yield various condensation products
(vii) Reducing property	Reduce Fehling's solution and ammoniacal $AgNO_3$ solution	Do not reduce Fehling's solution or ammon. $AgNO_3$ solution
(viii) Schiff's test	Respond to Schiff's test	Do not easily respond to Schiff's test

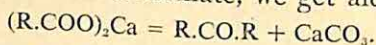
General methods of preparation.—(1) By the oxidation of secondary alcohols with acid dichromate or, by passing alcohol vapour over alumina or thoria at about 300° .



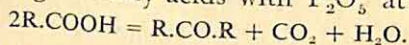
(2) By hydrolysing dihalogen derivatives of the type $R_1\text{CCl}_2R_2$.



(3) By the dry distillation of Ca, Ba or Pb salts of carboxylic acids alone. With two different salts, three ketones, two simple and one mixed, result. If one be a formate, we get aldehydes.



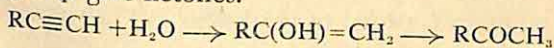
(4) By heating higher fatty acids with P_2O_5 at about 200° .



(5) By passing the vapour of a fatty acid (except formic acid) over manganous oxide at 300° .



(6) Homologues of acetylene passed into hot dilute H_2SO_4 in presence of $HgSO_4$, give ketones.



General properties.—Lower ketones up to C_{11} are mobile liquids, neutral and volatile; the higher ones are solids. The lower members are soluble in water but as the size of the hydrocarbon chain increases, solubility decreases rather rapidly. Ketones are, however, soluble in common organic solvents such as alcohol, ether, etc. They are lighter than water, having sp. gr. near about 0.8. Physical properties such as m.p., b.p., density, etc., change with rise in mol. wts. Unlike alcohols ketones cannot associate by hydrogen bonding; they have lower b.p. than the corresponding alcohols. Ketones do not form ketals with alcohols (difference from aldehydes). All possess smell—some of which are quite pleasant. Ketones react with sodium bisulphite to give bisulphite compounds; with HCN to form cyanhydrins; with phenylhydrazine to yield phenylhydrazones, etc. On oxidation, they form acids with a fewer carbon atoms, and go back to secondary alcohols on reduction. Ketones under suitable conditions, yield various condensation products.

Dialdehydes have two $-\text{CHO}$ and **diketones** two $>\text{CO}$ groups; the simplest are glyoxal, $\text{OHC}\cdot\text{CHO}$ (p. 110), and diacetyl, $\text{CH}_3\text{CO}\cdot\text{CO}\cdot\text{CH}_3$, which gives butter its flavour. Ethylmethyl ketone, on oxidation with SeO_2 gives diacetyl, a yellow oil (b.p. 88°), soluble in water. Dimethylglyoxime, $\text{CH}_3\text{C}(\text{NOH})\cdot\text{C}(\text{NOH})\cdot\text{CH}_3$, is a delicate reagent for detecting and estimating nickel ion.

QUESTIONS

1. How would you obtain a specimen of pure acetaldehyde from ethyl alcohol? Describe briefly the chief characteristics of acetaldehyde and show that it differs from paraldehyde. Calcutta Uni. B.Sc., Pass. 1939.

2. How is acetone obtained? Give an account of its physical properties, and enumerate as many reactions as you can in which it takes part. In what respects does a ketone differ from an aldehyde? Allahabad Uni. B.Sc. Pass. 1934.

3. What is the relation between alcohols and aldehydes? How would you obtain one class from another? By what reactions can one distinguish between a *primary*, a secondary and a tertiary alcohol?

Dacca Uni. B.Sc. Ordinary, 1938.

4. How can you obtain pure acetone from pyroligneous acid? How can it be obtained from starch? State the properties and uses of acetone.

Calcutta Uni. B.Sc. Pass. 1941.

5. Starting from acetone how can the following be obtained: mesitylene, propylene, chloroform and pinacone? Give equations.

6. Compare and contrast the chemical properties of aliphatic aldehydes and ketones.

Bombay Uni. B.A., 1937.

7. Explain with illustration the terms 'condensation' and 'polymerisation'; give an account of some polymerisation and condensation products of formaldehyde, acetaldehyde and acetone.

Agra Uni. B.Sc. 1952.

8. How would you detect formaldehyde in dilute aqueous solution? How does it differ from other aliphatic aldehydes. What are its chief uses? What is formalin?

9. A compound X has 69.8% C and 11.6% H; it does not reduce Fehling's solution and on careful oxidation with excess of oxidising agent, gives only acetic acid. What is the structure of X?

10. How would you proceed to test whether an aqueous solution contains acetaldehyde, ethyl alcohol or acetone?

11. Write notes on:—(a) Cannizzaro reaction, (b) pinacolone, (c) aldol condensation, and (d) mesitylene.

12. Give two methods for the preparation of acetaldehyde and acetone. Compare and contrast their properties.

B.A. & B.Sc., 1941, Andhra Uni.

13. How is acetone manufactured? State its properties and uses.

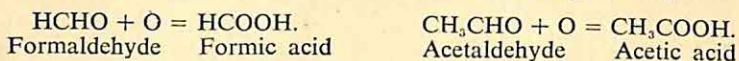
B.Sc. Degree Exam. 1942, Madras Uni.

14. A substance X has 69.8% C and 11.6% H with a vapour density of 43. With strong alkali it reacts as $2X + \text{NaOH} = Z + Y$ where $Z = X + 2H$ but does not turn brown or get polymerised. What is the probable structure of X?

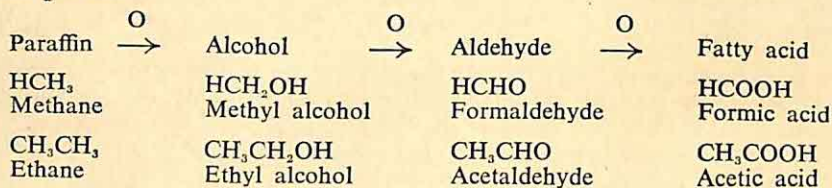
CHAPTER XIII

THE ALIPHATIC MONOBASIC ACIDS

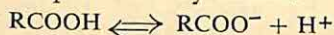
The fatty acids.—On oxidation, aldehydes take up another atom of oxygen and pass on to acids. Formaldehyde and acetaldehyde thus yield formic and acetic acid respectively.



The general formula for acids of this series may, therefore, be expressed as $\text{R}\cdot\text{COOH}$. The carboxyl (*carbonyl*, $-\text{CO}-$ and *hydroxyl*, $-\text{OH}$), $-\text{COOH}$, is the functional group of organic acids, excepting only a few, *e.g.*, hydrocyanic acid, sulphonic acids, phenols, etc. The carboxylic acids are apparently the final oxidation products of the paraffins:



Except formic acid, these may be regarded as derivatives of paraffins, in which one hydrogen atom has been replaced by a carboxyl group. These are called *fatty acids* because many of them occur in combination with glycerol in natural oils and fats, and resemble fats physically. Their acid character is due to the ionisable hydrogen of the carboxyl group, which is replaceable by metals.



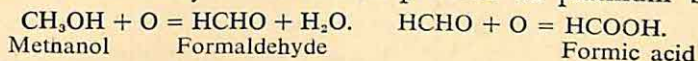
Basicity of a carboxylic acid is determined by the number of carboxyl groups in the molecule. Fatty acids are all monobasic; they are saturated or unsaturated according as the alkyl radical is saturated or not.

Nomenclature.—The trivial names of fatty acids end in “ic”, and are derived mostly from their original sources *e.g.*, formic acid (*formica*, ant), acetic acid (*acetum*, vinegar), butyric acid (*butyrum*, butter), etc. Valeric acid is present in *valerium* root, caproic, capric and caprylic acids occur in the fat of goat’s (*capra*) milk; lauric acid is found in the oil of *laurel*. Some of the higher members are named according to the number of carbon atoms in the molecule, *e.g.*, heptioic acid is $\text{C}_7\text{H}_{14}\text{O}_2$. The Geneva system names the acids after the parent hydrocarbon by adding ‘-oic acid’ to it, *e.g.*, HCOOH is methanoic acid; CH_3COOH is ethanoic acid, etc. This is, not, however, commonly followed.

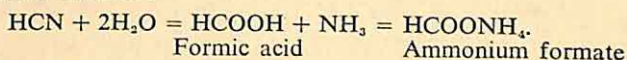
Formic acid, HCOOH , the first member of the series, occurs in red ants as also in the stings of bees and wasps which inject a little of it during stinging. It is present in some plants, *e.g.*, in

the bristles of stinging nettles and also in traces in urine, perspiration, etc. It has been known since 1670.

Preparation.—(1) Formic acid may be obtained by oxidising methanol or formaldehyde with air in presence of platinum black.



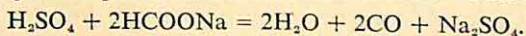
(2) Hydrocyanic acid, on hydrolysis with acids or alkalis, yields formic acid. An aqueous solution of hydrocyanic acid, on standing, forms ammonium formate.



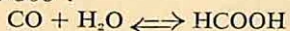
(3) Formic acid is manufactured by passing carbon monoxide (as producer gas) at 6-10 atmospheres pressure over soda-lime or sodium hydroxide at about 210°. The gas is slowly absorbed and sodium formate is formed. The free acid is liberated with cold *dilute* sulphuric acid:



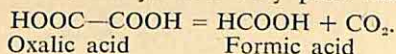
Strong H_2SO_4 decomposes the formate into carbon monoxide:



A recent industrial method claims to make the acid in 50% concentration by passing CO and steam under pressure over a metal oxide or halide catalyst at 200-300°.



(4) In the laboratory, formic acid is prepared by heating oxalic acid and glycerol. Heated alone, oxalic acid decomposes into formic acid and carbon dioxide; the yield is very poor due to side-reaction.



Preparation.—Take about 40 c.c. of glycerine and 50 g. of oxalic acid crystals in a distilling flask provided with a thermometer, a condenser and a receiver (Fig. 30). The bulb of the thermometer dips into the liquid. The

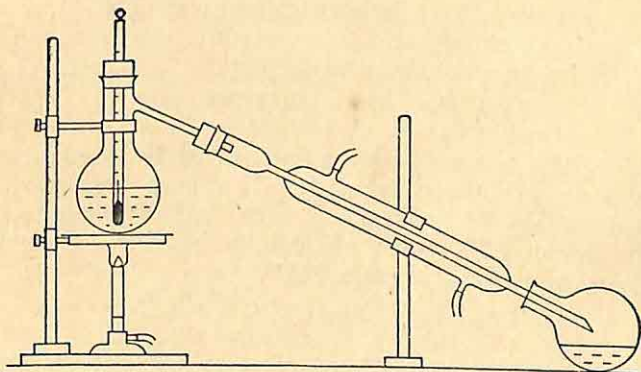
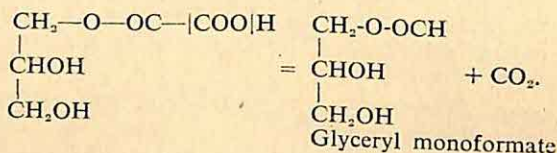
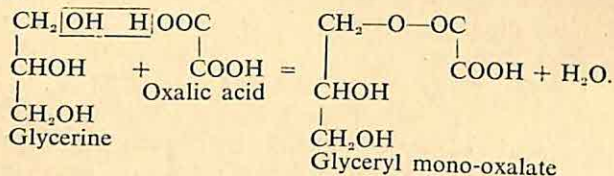


Fig. 30. Preparation of formic acid.

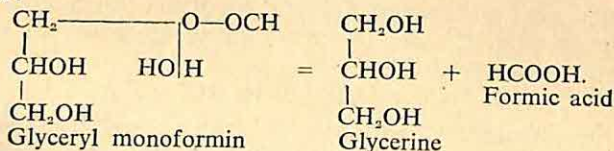
flask is heated to 100-110°. Carbon dioxide is evolved, and formic acid with water distils over. The action slackens after some time. More oxalic acid

crystals are added, maintaining the same temperature. This is continued until sufficient formic acid collects. The distillate is gently warmed with excess of litharge, PbO, and filtered hot. The filtrate is concentrated, colourless crystals of lead formate separate.

In presence of glycerine, the change takes place in a different way with a better yield. Glycerol mono-oxalate, first formed, decomposes into glyceryl mono-formate (or mono-formin) and CO_2 at higher temperature.

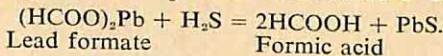


Fresh oxalic acid hydrolyses the monoformin to glycerol and formic acid:

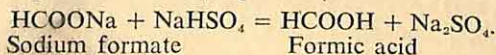


Regenerated glycerol then reacts with fresh oxalic acid and the process continues. A little glycerol converts a large amount of oxalic acid into formic acid (*cf.* ether, p. 119). Some glycerine is, however, transformed into allyl alcohol, $\text{CH}_2=\text{CH}\cdot\text{CH}_2\text{OH}$.

Anhydrous formic acid.—Formic acid (b.p. 100.5°) forms a constant-boiling mixture (b.p. 107.1°) with 22.5% water; so it cannot be purified by fractional distillation. Concentrated H_2SO_4 decomposes the acid. The anhydrous acid is commonly prepared by passing sulphuretted hydrogen over *dry* lead formate in a tube at about 110° .

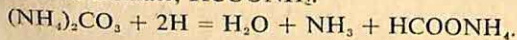


The acid is finally freed from sulphuretted hydrogen by distillation with a little fresh lead formate. The pure acid may also be obtained by distilling the sodium salt with sodium bisulphate, or the aqueous acid (about 85%) with phthalic anhydride (3 parts) which with water forms phthalic acid (m.p. 231°).

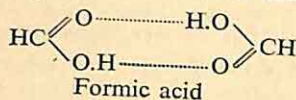


(5) Formic acid results when chloroform is treated with alcoholic NaOH (p. 79) or chloral with caustic alkalis (p. 78).

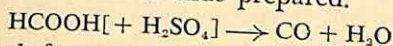
(6) Sodium amalgam reduces a concentrated solution of ammonium carbonate to ammonium formate, HCOONH_4 .



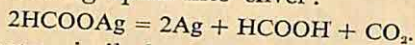
Properties.—Formic acid is a colourless, mobile liquid (sp. gr. 1.24 at 0°) with a pungent smell. It solidifies at 8.3°. It is a *dimer* in vapour state; a ring structure due to intermolecular bonding by hydrogen is supported by electron diffraction studies. Such bridged rings are called *chelate* rings (Greek *chela* a crab)



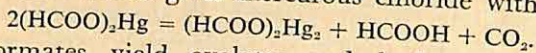
The acid is miscible with water, ether and alcohol in all proportions. It corrodes the skin raising blisters. Formic acid is the strongest fatty acid; it is about twelve times stronger than acetic acid. The dissociation constant, k (at 25°) is 21.4×10^{-5} for formic and 1.86×10^{-5} for acetic acid. It reddens litmus, liberates carbon dioxide from carbonates, and dissolves some metallic oxides. Formates are soluble in water except those of lead and silver. The acid and its salts are decomposed into carbon monoxide by concentrated H_2SO_4 which extracts the elements of water. Pure carbon monoxide is thus prepared.



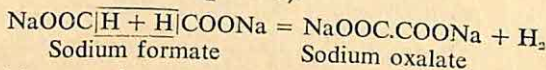
Formic acid and formates reduce ammoniacal AgNO_3 to silver (as does tartaric acid, q.v.) and also mercuric chloride to mercurous chloride. This is probably not due to an aldehyde group in them for they do not give other characteristic reactions of aldehydes *e.g.*, reduction of Fehling's solution. A soluble formate with AgNO_3 gives silver formate which on heating splits into silver:



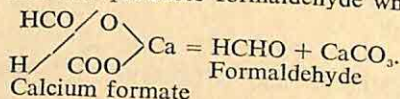
Mercuric formate, similarly formed, spontaneously decomposes to mercurous formate which gives mercurous chloride with chloride ions.



Alkali formates yield oxalates and hydrogen at about 400°. Oxalic acid is thus manufactured, sodium formate coming from carbon monoxide and caustic soda (p. 145).



But the calcium or zinc salt produces formaldehyde when heated:



Heated alone to 160°, it splits into carbon dioxide and hydrogen:



Uses.—Formic acid stimulates fermentation by yeast. It is an antiseptic for preserving fruit juice. In tanning, it is used for removing lime from leather, and in the textile industry for dyeing wool and cotton from an acid bath. It is also employed for coagulating rubber latex. Nickel formate is a catalyst for hydrogenating oils to *Vanaspathi*. Oxalic acid is made from sodium formate. The acid is used in nickel plating bath.

In 1955-56 India imported 3,535 cwt. of formic acid valued at Rs. 2,10,357.

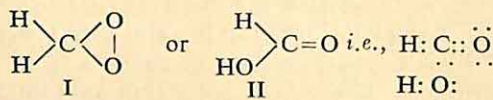
Tests.—(i) Neutral formates produce a red coloration with neutral ferric chloride solution (similar red coloration is also obtained with acetates which, however, differ from formates in the following tests).

(ii) Ammoniacal silver nitrate solution is reduced by formates.

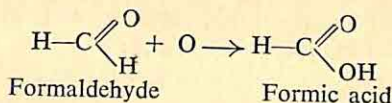
(iii) Mercuric chloride solution, added to a solution of formic acid or a formate, gives a white precipitate of mercurous chloride.

(iv) On warming anhydrous formic acid (or a solid formate) and conc. H_2SO_4 , carbon monoxide is liberated, which burns with a pale blue flame.

Constitution.—The molecular formula of formic acid is CH_2O_2 . With normal valencies of the atoms, formic acid may be either

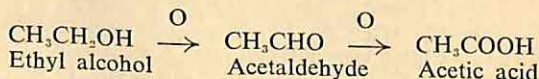


Formic acid which is monobasic, has only one replaceable hydrogen. Structure I has both the hydrogen similarly linked, both should be replaceable. This peroxide structure is inconsistent with its behaviour. The hydrogen of the $-\text{OH}$ group in II should be replaceable by metals as in sulphuric acid or alcohols, etc. Formation of formic acid by the oxidation of formaldehyde, or from chloroform and caustic soda (p. 79) follows readily from II which, therefore, represents the correct structure.

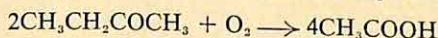
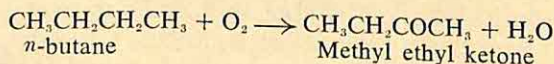


Acetic acid, CH_3COOH , known from the earliest times, is present in sour wine (as dilute vinegar) formed by the atmospheric oxidation of ethyl alcohol. In combination with glycerine, acetic acid occurs in croton oil; the free acid is found in the juice of many fruits and in animal secretions. As salts, it occurs in the sap of certain plants. Many essential oils contain esters of acetic acid.

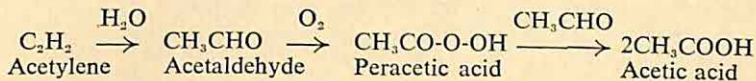
Preparation.—(1) By the oxidation of ethyl alcohol with potassium dichromate and sulphuric acid, or with air in presence of a catalyst, e.g., platinum black.



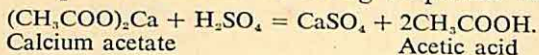
(2) In a more recent method, a mixture of large excess of *n*-butane (from petroleum) and air under pressure is passed into acetic acid containing cobalt and manganese acetates at 165° . Acetic acid and methylethyl ketone formed are dissolved in water and separated by fractional distillation.



(3) Glacial acetic acid is manufactured mainly from acetylene which with water yields acetaldehyde on passing into hot sulphuric acid (10-40%), containing mercuric sulphate (p. 67). Acetaldehyde is oxidised to acetic acid by air at about 70° in presence of manganous acetate (0.5%). Peracetic acid, first formed, reacts with acetaldehyde to give acetic acid. U. S. A. thus makes over 75% of her acetic acid (cf. formation of sodium acetate from acetylene, p. 68). The yield is over 80% and the strength about 97%.



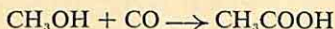
(4) From *pyroligneous acid* which contains about 6-10% acetic acid (p. 85). The vapour is passed into hot milk of lime—calcium acetate thus formed, is heated to about 250° in air to decompose some of the impurities, 'grey acetate of lime' is obtained. It is distilled with the requisite amount of strong sulphuric acid.



The distillate containing 40-60% of acetic acid, is neutralised with caustic soda. Sodium acetate, $\text{CH}_3\text{COONa} + 3\text{H}_2\text{O}$, formed is fused to anhydrous sodium acetate and distilled with conc. H_2SO_4 to obtain pure glacial acetic acid. Crude calcium acetate, distilled *in vacuum* with conc. H_2SO_4 , gives 80% acetic acid which is fractionated to 99.995% acid.

A cheaper method of extracting acetic acid from pyroligneous acid with high-boiling wood oil (the Suida process) or isôpropyl ether competes with the synthetic process. The solvent is recovered by fractional distillation and used again. 92% acetic acid is thus obtained. This meets only a small fraction of the world demand.

(5) Methanol vapour and a large excess of CO under 700 atmospheres are combined at 300-400° in presence of a catalyst (tungsten or a phosphate) to acetic acid and methyl acetate.



(6) Heated to 180° in an atmosphere of CO, sodium methoxide forms sodium acetate (cf. formation of sodium formate from NaOH and CO, p. 145) which gives acetic acid with H_2SO_4 . Boiling mineral acids or alkalis hydrolyse methyl cyanide to acetic acid.



(7) Dilute acetic acid as 'Vinegar' is obtained by fermenting weak alcohol with a living organism, *Mycoderma aceti*, in presence of air. It is a case of bacterial oxidation which also takes place in presence of other oxidants (e.g., quinone) than air. The spores of these bacteria, present in air, gradually convert light wines into acetic acid; wines thus go sour. They cannot, however, survive in wines containing more than 15% alcohol. That is why port and sherry do not turn sour in air. They cannot also grow in *pure* alcohol, because they need food materials like phosphates, nitrogenous matters, etc., present in wine.

Pasteur's *Mycoderma aceti* no longer stands for a particular species of bacteria and so the name has been abandoned. *Acetobacter aceti*, *A. pasteurianum*, etc., are distinct species capable of effecting the change.

Quick vinegar process.—Dilute alcohol (6-10%) e.g., low-grade wines or fermented wort, is allowed to trickle down beech-wood shavings, birch twigs, wood charcoal or fabrics, previously moistened with vinegar, so that these are coated with the growth of the organism. The shavings are placed in large wooden vats with two perforated discs at the top and bottom. There are holes on the side of the vat near the bottom to admit an ascending current of air while the alcoholic liquor travels downwards. The shavings distribute the wine over a large surface, facilitating oxidation,

and also provide food for the bacteria. As the reaction is exothermic, the rate of flow of alcohol is regulated to keep the temperature near about 35° . The supply of air is controlled—with a very slow current, oxidation proceeds only up to acetaldehyde, whereas with too liberal a supply, carbon dioxide and water may result. The liquor that collects in the receiver is allowed to drop again from the top of the vat. By repeating the process, vinegar containing about 14% acetic acid may be obtained. At a higher

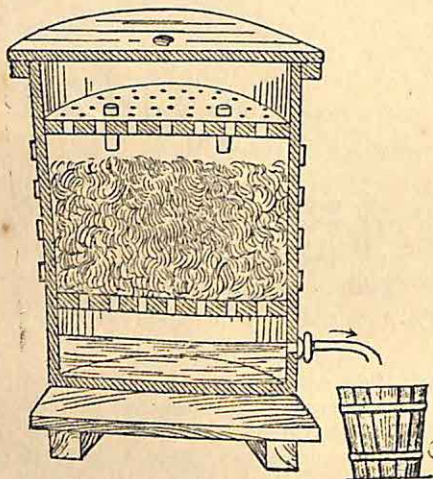


Fig. 31. Manufacture of vinegar.

concentration, the bacteria become inactive. Vinegar usually, however, contains only 4-8% of acetic acid. *Malt vinegar* is made from fermented wort. Besides acetic acid, vinegar contains a little alcohol, some tartaric and succinic acids, and also a little of their ethyl esters which partly account for its odour. Commercial acetic acid is seldom made from vinegar—it is too dilute.

Properties.—Acetic acid is a colourless liquid with a pungent smell. It boils at 118° and has a specific gravity 1.055 at 15° . It solidifies to an ice-like, crystalline solid at 16.7° , hence the name *glacial* (Latin *glacies* ice) acetic acid. The acid is miscible with water, alcohol and ether in all proportions. It dissolves in water with evolution of heat and contraction in volume so that an aqueous solution may have a higher density than the acid itself. It burns with a pale blue flame near about its boiling point. Acetic acid is a good solvent for many organic substances and also for phosphorus, iodine and sulphur. It attacks the skin causing painful wounds.

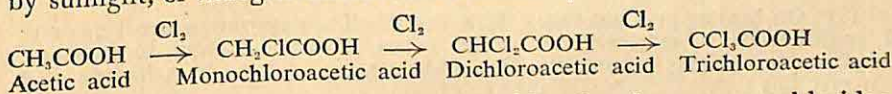
Salts of acetic acid or acetates are mostly crystalline. Normal acetates are soluble in water but the basic salts are mostly insoluble.

Sugar of lead, $(\text{CH}_3\text{COO})_2\text{Pb} + 3\text{H}_2\text{O}$, obtained by dissolving litharge or lead carbonate in the commercial acid, has a sweet, astringent taste and is a poison. It is used in medicine and dyeing.

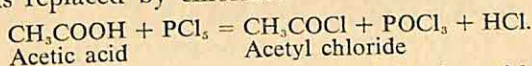
Acetic acid is weak, much weaker than HCl , HNO_3 , etc. The dissociation constant, k of acetic acid at 25° is only 1.86×10^{-5} . (The degree of electrolytic dissociation in decinormal solution at 25° is 91% for HCl but only 1.3% for acetic acid and 0.17% for H_2CO_3). k of acetic acid in H_2O is about 3 times that in heavy water, D_2O . It decomposes carbonates liberating carbon dioxide and reacts with some metals with evolution of hydrogen. Zinc dust in acetic acid is a common reducing agent. Acetic acid is a dimer, $(\text{CH}_3\text{COOH})_2$, in benzene solution and also in vapour or liquid form. This association is due to hydrogen bonding (cf. formic acid, p. 147).

In contrast with formic acid, acetic acid is very weak, non-reducing, stable to heat or conc. H_2SO_4 and has no antiseptic property.

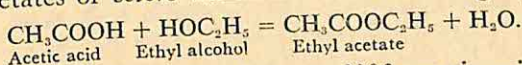
Acetic acid is remarkably stable towards oxidising agents; so it is used as a solvent in oxidation reactions. Lithium aluminium hydride, LiAlH_4 , in ether solution reduces it to ethyl alcohol. On passing chlorine into the boiling acid, the hydrogen atoms of the methyl group are successively replaced by chlorine, we get mono-, di- and tri-chloroacetic acid and HCl . Bromine acts similarly. The process is accelerated by sunlight, or halogen carriers like P , S or I_2 .



Acetic acid gives acetyl chloride with phosphorus pentachloride; the $-\text{OH}$ group is replaced by chlorine.



With alcohols in presence of strong sulphuric acid, acetic acid forms alkyl acetates or *esters* which are sweet-smelling liquids.



Passed over aluminium phosphate at 600° , acetic acid forms ketene (p. 136). $\text{CH}_3\text{COOH} \rightarrow \text{CH}_2=\text{CO} + \text{H}_2\text{O}$.

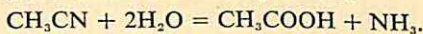
Uses.—Alkali acetates are diuretics in medicine; a solution of basic lead acetate is employed in fractures and burns. Acetic acid is used in dyeing and for making acetone, acetyl chloride, acetic anhydride, phenacetin, aspirin, etc. Aluminium and chromic acetates are mordants in dyeing; aluminium acetate makes fabrics water-proof. Basic copper acetate is the pigment *verdigris*. *Schweinfurter* or *Paris green*, an insecticide, is a double salt of copper acetate and arsenite, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 3\text{Cu}(\text{AsO}_2)_2$. Cellulose acetate forms acetate rayon. Acetic acid is employed for coagulating rubber from latex. Manganese acetate is a paint dryer; lead tetraacetate, $\text{Pb}(\text{CH}_3\text{COO})_4$, is an important oxidant. Vinegar is chiefly used for table purposes and for making white lead, sugar of lead, etc.

In 1955-56 India imported 25,421 cwt. of acetic acid valued at Rs. 20,18,979. A fairly large quantity is now made in India. Ethyl alcohol from molasses may be the main source. U.S.A. made 524 million lb. of acetic acid in 1955.

Constitution.—(1) The molecular formula of acetic acid is $C_2H_4O_2$. (2) It is mono-basic, sodium acetate is $C_2H_3O_2Na$. Other three hydrogen atoms, not replaced by metals, are differently linked. (3) PCl_5 gives acetyl chloride, C_2H_3OCl , and HCl , an $-OH$ being replaced by chlorine (cf. action of PCl_5 on alcohol, p. 92).



(4) Chlorine substitutes three hydrogen atoms in acetic acid, giving trichloro-acetic acid, $C_2Cl_3O(OH)$, which forms a sodium salt with $NaOH$ and a chloro-derivative with PCl_5 . The hydrogen of the hydroxyl group is, therefore, salt-forming. (5) Formation of acetic acid from methyl cyanide by hydrolysis shows that the two carbon atoms are directly linked.



Methyl cyanide Acetic acid

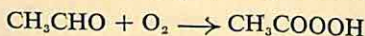
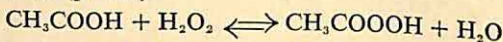
The three hydrogen atoms, replaceable by chlorine, are linked to the same carbon as sodium methide, CH_3Na , when heated with CO_2 , yields sodium acetate, CH_3COONa . Acetic acid, therefore, is $CH_3CO.OH$.

Tests.—(1) Neutral ferric chloride gives a deep red coloration with the solution of a neutral acetate. On boiling, a brown precipitate of basic ferric acetate is obtained. Acetic acid does not reduce mercuric chloride or ammoniacal silver nitrate (cf. formic acid, p. 148).

(2) Acetic acid or acetates, when heated with ethyl alcohol and strong H_2SO_4 , produce ethyl acetate which has a pleasant odour.

(3) On heating in a test-tube a little dry alkali acetate with a small quantity of arsenious oxide, extremely nauseating odour of cacodyl oxide is produced. The fumes are highly poisonous. But other organic acids such as butyric acid also give this test.

Peracetic acid, CH_3COOOH , is made by acetylating 90% H_2O_2 with acetic acid in presence of 1% H_2SO_4 at room temperature, or by the autoxidation of acetaldehyde at 0° in air (p. 127).



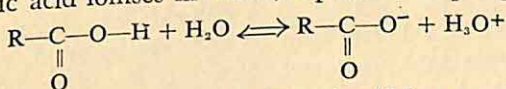
It is a colourless, toxic liquid (b.p. 110°), miscible with water. It is weaker ($pK = 8.2$) than acetic acid ($pK = 4.73$) and is used as an oxidant in organic syntheses, for bleaching textiles at neutral pH and as a germicide.

Acidity of carboxylic compounds.—When a hydrogen atom of water is replaced by an alkyl group, the ionisation constant of the resulting alcohol, ROH , falls to about 10^{-17} from 10^{-14} for water at ordinary temperature. Alcohols are weaker 'acids' than water. If the hydrogen of water be substituted by an acyl group, $RCO-$, the ionisation constant of the carboxylic compound, $RCO.OH$, formed rises to about 10^{-5} . Carboxylic compounds are much stronger 'acids' than water. During ionisation, a proton gets detached from the acid (broadly, an acid is a substance that can donate a proton, and a base is one that can accept a proton) and the shared electron pair between the oxygen and hydrogen atoms of the OH group remains with the oxygen. Electrophilic atoms or groups, attached to the oxygen of OH group, have a tendency to attract electrons from the oxygen; they, therefore, facilitate the separation of the proton. Nucleophilic atoms or groups, on the other hand, tend to repel electrons towards the oxygen

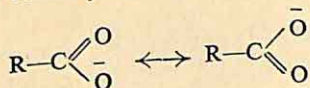
of OH group; the proton is consequently more firmly bound to oxygen. It will, therefore, have a lesser tendency to leave the oxygen. Now, in alcohols, the electron-repelling alkyl group helps retaining the hydrogen of the OH group to the oxygen; the result is a smaller ionisation. The

electron attracting acyl group, $\text{R}-\text{C}(=\text{O})$, in carboxylic compounds helps the escape of a proton from the OH group (the oxygen atom of the CO group having a greater nuclear charge, pulls the electrons away from the carbon, making it deficient in electrons). The result is a greater ionisation.

A carboxylic acid ionises in water, a proton-accepting solvent, as



and the residual carboxylate ion stabilises itself by resonance (p. 106):



The re-combination of the proton and the carboxylate ion is made more difficult. The normal state of the carboxyl group is an inter-

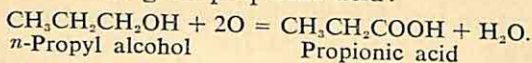
mediate between $\text{R}-\text{C}(=\text{O})-\text{O}-\text{H}$ and $\text{R}-\text{C}(\text{O}^+)=\text{O}-\text{H}$ with a

partial positive charge on the oxygen of the OH group and a partial negative charge on the oxygen of the CO group. This explains why the doubly-linked oxygen atom of the carboxyl group does not exhibit normal ketonic properties such as reacting with HCN, phenylhydrazine, etc. X-ray analysis shows that in acetic acid, the hydrogen atom of the carboxyl group lies midway between the two oxygen atoms. The replacement of hydrogen of CH_3 group in acetic acid by chlorine increases the acidity of chloroacetic acid (p. 102) due to the inductive effect of the electrophilic chlorine atom; a similar effect is produced by the substitution of the CH_3 group in acetic acid by hydrogen, formic acid is considerably stronger than acetic acid. The length of the hydrocarbon chain in an alkyl group has, however, little effect on the strength of a fatty acid; thus the dissociation constant, k , of caprylic acid, $\text{C}_7\text{H}_{15}\text{COOH}$, is 1.45×10^{-5} while that of propionic acid, $\text{C}_2\text{H}_5\text{COOH}$, is 1.43×10^{-5} . Vicinal alkyl groups diminish the strength of aliphatic acids, e.g., trimethylacetic acid, $(\text{CH}_3)_3\text{C.COOH}$, ($k = 0.92 \times 10^{-5}$) is weaker than acetic acid, CH_3COOH , ($k = 1.86 \times 10^{-5}$).

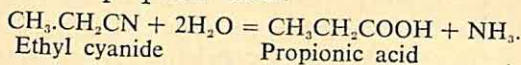
The strength of an acid is sometimes more conveniently expressed by its pk value which is the negative logarithm of its dissociation constant k (i.e., $\text{pk} = -\log k$). The pk value for acetic acid ($k = 1.86 \times 10^{-5}$) is $-(-5 + 0.27)$ or 4.73. The lower the pk value, the stronger the acid.

Propionic acid, $\text{CH}_3\text{CH}_2\text{COOH}$, occurs in small amounts in pyroligneous acid and in the sweat of rheumatic patients. It was obtained as a by-product in the extraction of potash from kelp by

fermentation during the first world war. Oxidation of *n*-propyl alcohol with dichromate mixture gives propionic acid:



Ethylene, carbon monoxide and water combine directly under pressure to form propionic acid ('oxo' process). Hydrolysis of ethyl cyanide also produces propionic acid:



Propionic acid is a liquid (b.p. 141°) with a pungent smell, resembling acetic acid. It mixes with water, ethanol and ether in all proportions but with solid calcium chloride or other salts, it can be 'salted out' as an oily layer from its aqueous solution, whence its name which means 'first fat.' It is not, however, found in fats. Propionates are soluble in water; calcium propionate is added to bread dough to delay mould formation.

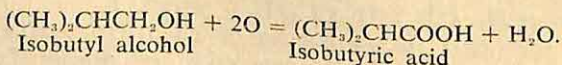
Butyric acids, $\text{C}_3\text{H}_7\text{COOH}$.—Isomerism first occurs with fatty acids containing four atoms of carbon, and two butyric acids are known—normal and iso-.

Normal butyric acid, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$.—Butter contains 2.5% of glyceride of *n*-butyric acid. The disagreeable smell of rancid butter is due to the free acid. It occurs free in perspiration, the juice of muscles and some fats and oils. The acid may be obtained by the general methods on page 155. But it is usually made by fermenting sugars or starch with *Bacillus butylicus* present in sour milk or decaying cheese (butyric fermentation). Starch is hydrolysed to glucose which is fermented to lactic acid. The latter finally yields butyric acid, carbon dioxide and hydrogen. During fermentation, chalk is added to neutralise the acid formed, as in strongly acid media, the ferment becomes inactive. The temperature is kept at 35° - 40° . Calcium butyrate formed is decomposed by hydrochloric acid and the free acid obtained by distillation.



Butyric acid is a thick, sour liquid (b.p. 162°) with the smell of rancid butter or stale perspiration. It is miscible with water, and can be obtained as an oil from aqueous solution, like propionic acid, with calcium chloride. The acid is volatile in steam. Ethyl butyrate, having the odour of pine-apple, is an essence. The acid is used in tanning for removing lime from leather. Calcium butyrate is *less* soluble in hot water than in cold; this helps its separation and identification.

Isobutyric acid, $(\text{CH}_3)_2\text{CHCOOH}$, occurs free and as sweet-smelling esters in some plants. It is prepared by the oxidation of isobutyl alcohol:



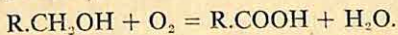
Isobutyric acid (b.p. 154°) resembles the normal isomer closely, but is more easily oxidised. It is slightly soluble in water, and unlike the normal butyrate of calcium, the iso-salt is more soluble in hot water than in the cold.

Valeric acids, $C_5H_{10}O_2$, four in number, are all known, *n*-valeric acid, $CH_3CH_2CH_2CH_2COOH$, (b.p. 187°) occurs in pyroligneous acid; it may be made by oxidising *n*-primary amyl alcohol. This and isovaleric acid, $(CH_3)_2CH.CH_2COOH$, (b.p. 175°) occur in valerian root. Isovaleric acid may be obtained by oxidising iso-amyl alcohol. Ammonium valerate is a sedative.

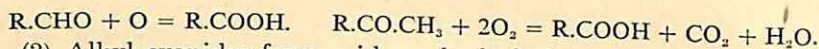
Higher fatty acids.—Of these, the normal acids with an even number of carbon atoms occur in nature as esters with lower alcohols in the ethereal oils of plants; as glycerides in fats and oils, and as esters of higher monohydric primary alcohols in waxes. Starting with butyric acid, practically all the higher members can be obtained, in more or less pure state, by the hydrolysis of fats or oils. No oil or fat is a single glyceride—it is, as a rule, a mixture. Different fats usually contain glycerides of different acids, but those of palmitic acid, $C_{16}H_{32}O_2$, stearic (Greek *stear* tallow) acid, $C_{18}H_{36}O_2$, and oleic acid, $C_{18}H_{34}O_2$, occur in most of them. Butter fat contains glyceride of butyric acid; goat's fat, glycerides of caproic, caprylic and capric acids. Glyceride of stearic acid or 'stearin' predominates in beef and mutton tallow; that of palmitic acid is the main constituent of palm oil, while olive oil chiefly consists of the glyceride of the unsaturated oleic acid. All these acids have straight carbon chains. The saturated acids are waxy solids while the unsaturated ones are usually liquids. Free solid acids, e.g., stearic acid, are used in candle manufacture. During the last war the Germans converted the hydrocarbons obtained by Fischer-Tropsch process into higher fatty acids (containing both odd and even number of carbon atoms) by catalytic oxidation. These were made into soap and also margarine (after being converted into glycerides). Sodium or potassium salts of higher fatty acids are *soaps*. Beeswax, spermaceti, etc. are palmitic esters of higher alcohols such as cetyl alcohol, $C_{16}H_{33}OH$.

Higher fatty acids with an odd number of carbon atoms seldom occur in natural fats and oils. They can be obtained from acids with an even number of carbon atoms by converting them into ketones and oxidising the latter. In properties, higher fatty acids resemble acetic acid but they are less reactive. *Zinc stearate*, a bulky powder, is used as a mild antiseptic in ointments and dusting powders. *Sodium stearate* is largely employed in 'hardening' glycerine for suppositories, in vanishing face creams, and shaving creams. Copper soaps are excellent fungicides.

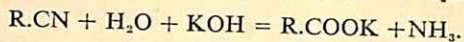
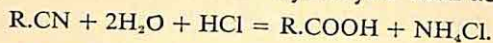
General methods of preparation.—(1) By the oxidation of primary alcohols with air in presence of a catalyst e.g., platinum, or with chromic acid, and in some cases with micro-organisms (cf., preparation of acetic and butyric acids):



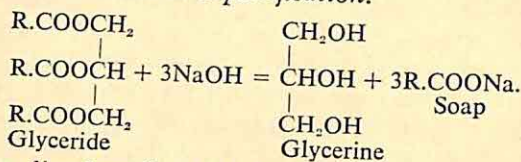
(2) Aldehydes and ketones yield, on oxidation, mono-carboxylic acids. Ketones give acids with a fewer carbon atoms (p. 137).



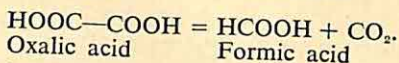
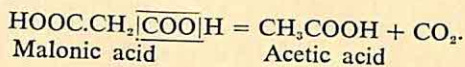
(3) Alkyl cyanides form acids on hydrolysis with acids or alkalis:



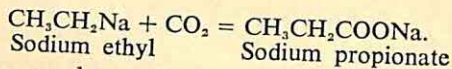
(4) Higher fatty acids are obtained by the hydrolysis of oils and fats with mineral acids or alkalis. Alkaline hydrolysis is done in making soaps and is known as *saponification*.



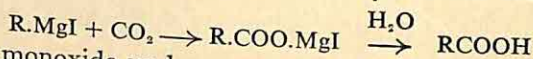
(5) When a dicarboxylic acid, having two -COOH groups attached to the *same* carbon, is heated strongly, a monocarboxylic acid is formed. Thus malonic acid gives acetic acid and carbon dioxide; oxalic acid behaves similarly:



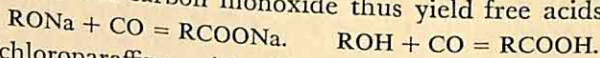
(6) Sodium alkyls react with carbon dioxide yielding sodium salts of monocarboxylic acids; metal alkyls are, however, difficult to prepare and also very unstable.



(7) By passing carbon dioxide into magnesium alkyl halide (*Grignard compound*) in ether at low temperature and treating the product with dilute hydrochloric acid, carboxylic acids are obtained:



(8) Carbon monoxide under pressure reacts at 160-200° with sodium alkoxides producing sodium salts of lower fatty acids; with acid catalysts, alcohol and carbon monoxide thus yield free acids.



(9) Trichloroparaffins, with all the chlorine atoms linked to the *same* carbon, on hydrolysis, yield fatty acids. Chloroform gives formic acid (p. 79).

(10) Fatty acids may be obtained from malonic and acetoacetic ester, and their derivatives (q.v.). By oxidising hydrocarbons (e.g., from petroleum or Fischer-Tropsch process) of moderately high b.p. with air in presence of manganous stearate at 120°, a mixture of higher fatty acids is made industrially for conversion into soap.

General properties.—Lower members of the series are corrosive liquids with a pungent smell and sour taste. They are miscible with water in all proportions and distil without decomposition. They turn litmus red, readily liberate carbon dioxide from carbonates and are

volatile in steam. The middle members (C_4 — C_9) possess a rancid smell, are oily liquids and immiscible with water. The higher members beginning with C_{10} are colourless solids without odour, resembling paraffin wax in appearance. They are insoluble in water, and can be distilled only under diminished pressure. They hardly affect litmus, their dissociation constants being very small.

Fatty acids are practically colourless and readily soluble in alcohol or ether. They are reduced to primary alcohols by lithium aluminium hydride and to paraffins on heating with hydrogen under pressure to a high temperature in presence of nickel. All except formic acid are stable towards oxidising agents. As in a homologous series, there is a gradation of properties as the molecular weight increases. Thus solubility in water, and sp. gr. decrease as we go higher up in the series. The boiling point rises for each $-CH_2-$ group by about 19° in the case of normal acids. But generally normal acids, with odd number of carbon atoms, have a *lower* m.p. than the preceding normal member with an even number. The C-atoms of a *n*-fatty acid chain form a zig-zag arrangement as shown by X-ray diffraction; the $-COOH$ and CH_3- at the ends in odd carbon acids lie on the same side whereas those in even carbon acids are on opposite sides. The latter makes a more stable crystal lattice resulting in a higher m.p. The low volatility of lower members is due to association through hydrogen bonding (cf. alcohols, p. 94). C_8 to C_{12} fatty acids possess insecticidal toxicity, hence the use of soaps as insecticide.

The Fatty acids, $C_nH_{2n}O_2$.

Name	Formula	m.p. $^\circ C$	b.p. $^\circ C$	sp. gr. at 25°	$k \times 10^5$ at 25°
Formic	HCOOH	8.3	100.5	1.213	21.4
Acetic	CH_3COOH	16.5	118.1	1.044	1.8
<i>n</i> -Propionic	C_2H_5COOH	—22	141	.988	1.4
<i>n</i> -Butyric	C_3H_7COOH	—5.5	162	.954	1.5
<i>n</i> -Valeric	C_4H_9COOH	—34.5	186	.940	1.6
<i>n</i> -Caproic	$C_5H_{11}COOH$	—3.5	205	.924	1.4
<i>n</i> -Heptylic	$C_6H_{13}COOH$	—10.5	223	.920	—
<i>n</i> -Caprylic	$C_7H_{15}COOH$	—16.5	236	.906	—
<i>n</i> -Nonylic	$C_8H_{17}COOH$	12.5	254	.905	—
<i>n</i> -Capric	$C_9H_{19}COOH$	31	269	.886	—
<i>n</i> -Lauric	$C_{11}H_{23}COOH$	43	180 (16 mm.)	.858	—
Palmitic	$C_{15}H_{31}COOH$	62	268 (100 mm.)	.848	—
Stearic	$C_{17}H_{35}COOH$	69.4	287	.840	—

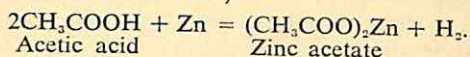
Reactions.—(1) The fatty acids form salts with carbonates, bicarbonates or hydroxides, which are not appreciably hydrolysed by water.



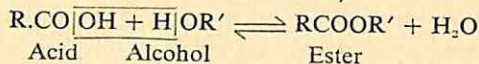
(2) The acids have a strong tendency to associate, often to a dimer. They, therefore, form acid salts, such as acid sodium acetate.



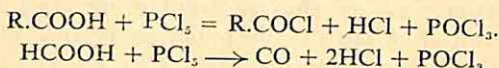
(3) Metals such as zinc replace the hydrogen of the carboxyl group (especially in the lower members):



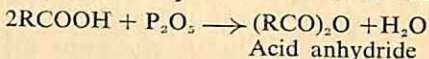
(4) On heating fatty acids with alcohols in presence of dehydrating agents, *esters* are formed (*vide* Chapter XV).



(5) Fatty acids yield *acid chlorides*, RCOCl , with phosphorus pentachloride or thionyl chloride, chlorine replacing the $-\text{OH}$ group. Formic acid gives CO and HCl .



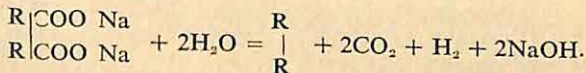
(6) Strong dehydrating agents such as phosphorus pentoxide extract one molecule of water from two molecules of acid (*cf.*, formation of ethers, p. 118); *acid anhydrides* are thus formed:



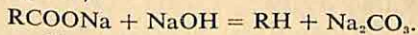
(7) The carboxyl group is difficult to reduce. Hydrogen under high pressure in presence of nickel or copper at about 400° , or phosphorus with hydriodic acid, reduces fatty acids to alcohols and sometimes to paraffins. They are, however, readily and quantitatively reduced to alcohols by lithium-aluminium hydride, LiAlH_4 , in ether solution. Esters are easily reduced to alcohols with sodium and alcohol.



(8) Their alkali salts in aqueous solution, on electrolysis, give paraffins (*cf.*, formation of ethane from alkali acetate, p. 44). Alkane and CO_2 go to the anode.



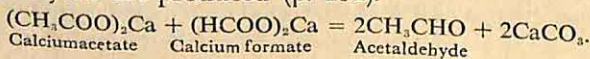
(9) Alkali salts of fatty acids, on *dry distillation* with soda-lime, yield paraffins, RH , (p. 49):



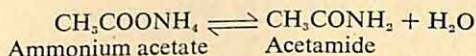
(10) By the *dry distillation* of calcium salt of fatty acids (except formic acid), ketones are obtained (p. 135). By taking two different calcium salts, mixed ketones can be prepared together with simple ketones. Ketones also result when vapour of a fatty acid is passed over thoria or manganous oxide at $400\text{--}450^\circ$.



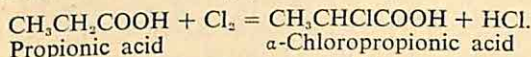
(11) By heating the calcium salt of an acid with calcium formate, both dry, aldehydes are produced (p. 132).



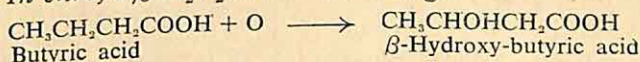
(12) Ammonium salts of fatty acids, on distillation, yield *acid amides*—the -OH group of the acid being replaced by the amido, -NH₂, group. Dissociation into the acid and NH₃ also occurs.



(13) Under the influence of sunlight and heat and also in presence of catalysts, chlorine or bromine attacks the alkyl radical of fatty acids, producing halogen-substituted acids. The hydrogen attached to the α -carbon (*i.e.*, next to the carboxyl) is thus replaced.



(14) In our system, fatty acids are oxidised at the β -position. Diabetic patients can convert butyric acid into β -hydroxy-butyric acid but not further. *In vitro*, 3% H₂O₂ effects this change.



(15) Silver salts of fatty acids react with Br₂ or I₂ in dry CCl₄ to give alkyl bromide or iodide:



QUESTIONS

- How is formic acid prepared in the laboratory as well as on a large scale? Give its important reactions and tests. B.Sc., 1941, Agra University.
- What are the usual methods for the manufacture of acetic acid? Establish its structural formula.
- What substances can be obtained from calcium salts of fatty acids? Give equations.
- How may a sample of pure formic acid be obtained from (a) CO, (b) oxalic acid?
- Justify: "Formic acid is not a typical fatty acid."
- Starting from ethyl alcohol, how can you prepare a sample of propionic acid?
- Give a method for separating the following from a mixture—methyl alcohol, acetone and acetic acid.
- Indicate two processes by which acetic acid is manufactured. Starting from acetic acid, how would you prepare trichloro-acetic acid, acetyl chloride and acetic anhydride? (Dacca Uni. B.Sc., Pass, 1933).
- Name the sources of formic acid. How is the anhydrous acid prepared? In what way is the acid related to HCN? Give reasons for your answer. (Cal. Uni. B.Sc., Pass, 1931).
- Indicate how, starting from methane, you may prepare acetic acid. (Cal. Uni. B.Sc., Pass, 1938).
- How is acetic acid manufactured by fermentation? How would you obtain a sample of pure glacial acetic acid? State its properties and uses. (Cal. Uni. B.Sc., Pass, 1938).
- How is glacial acetic acid manufactured? Describe a method by which you can concentrate dilute acetic acid to the anhydrous state. (B.A. and B.Sc. Degree Examination, 1935, Andhra University.)

CHAPTER XIV

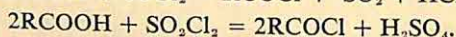
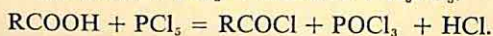
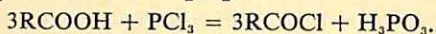
THE DERIVATIVES OF FATTY ACIDS—I.

ACID CHLORIDES, ACID ANHYDRIDES AND ACID AMIDES

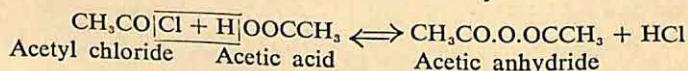
Different derivatives are formed from fatty acids by replacing the hydrogen or the hydroxyl of the carboxyl group or the hydrogen of the alkyl group by different groups or atoms, *e.g.*, CH_3COOEt , CH_3COCl , CH_2ClCOOH , $\text{CH}_2(\text{CN}).\text{COOH}$, etc. The derivatives obtained by substitution in the carboxyl group are apparently similar to those from monohydric alcohols; in these, the monovalent R.CO- , called *acyl group*, remains intact. ($\text{CH}_3\text{CO-}$ is acetyl, $\text{CH}_3\text{CH}_2\text{CO-}$ propionyl and so on).

$\text{CH}_3\text{CH}_2\text{OH}$	Ethyl alcohol	$\text{CH}_3\text{CO.OH}$	Acetic acid
$\text{CH}_3\text{CH}_2\text{ONa}$	Sodium ethylate	CH_3COONa	Sodium acetate
$\text{CH}_3\text{CH}_2\text{Cl}$	Ethyl chloride	$\text{CH}_3\text{CO.Cl}$	Acetyl chloride
$\text{CH}_3\text{CH}_2\text{>O}$	Diethyl ether	$\text{CH}_3\text{CO>O}$	Acetic anhydride
$\text{CH}_3\text{CH}_2\text{NH}_2$	Ethylamine	CH_3CONH_2	Acetamide

Acid chlorides, R.COCl .—If the -OH of the carboxyl group of an acid be replaced by chlorine, we get an *acyl* or *acid chloride*, R.COCl . This is done with phosphorus tri- or penta-chloride, thionyl chloride, SOCl_2 , or sulphuryl chloride, SO_2Cl_2 .



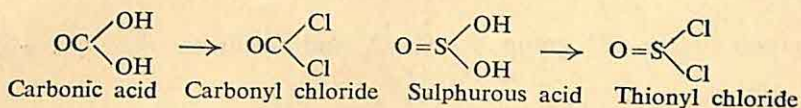
Salts of acids react similarly and being cheaper, are employed industrially for making acid chlorides. A side-reaction between the acid and acid chloride gives some acid anhydride:



Heated under pressure with copper catalyst, an alkyl halide and carbon monoxide form acid chloride: $\text{CH}_3\text{Cl} + \text{CO} = \text{CH}_3\text{COCl}$. It is not yet an industrial process. Thionyl chloride (b.p. 79°) gives a higher yield and is more convenient, as both SO_2 and HCl , being gases, are readily removed. Acid chlorides are technically made with thionyl chloride or sulphuryl chloride.

The acid halides are named after the parent acids by changing the ending *ic* to *yl*; *e.g.*, CH_3COCl is acetyl chloride; $\text{CH}_3\text{CH}_2\text{COCl}$ propionyl chloride, and so on. The I. U. C. (International Union of Chemistry in 1922 at Geneva) system names them ethanoyl, propanoyl, butanoyl chloride.

There are inorganic acid chlorides also. For example,



Formyl chloride, HCOCl , obtained from chlorine and formaldehyde at -80° , is too unstable to exist at ordinary temperature. The most important is acetyl chloride, CH_3COCl .

Preparation of acetyl chloride.—40 c.c. of glacial (anhydrous) acetic acid are taken in a distilling flask fitted with a tap-funnel, a condenser and a receiver. The latter is joined to a tower of soda-lime to absorb the hydrochloric acid, and also to guard against in-coming moisture which decomposes acetyl chloride (Fig. 32). 25 c.c. of PCl_5 are slowly added from the tap-funnel. The flask is gently warmed on water-bath to about 50° , practically all the HCl escapes. The temperature is raised, acetyl chloride distils at 55° leaving behind the non-volatile phosphorous acid. It is purified by re-distillation.

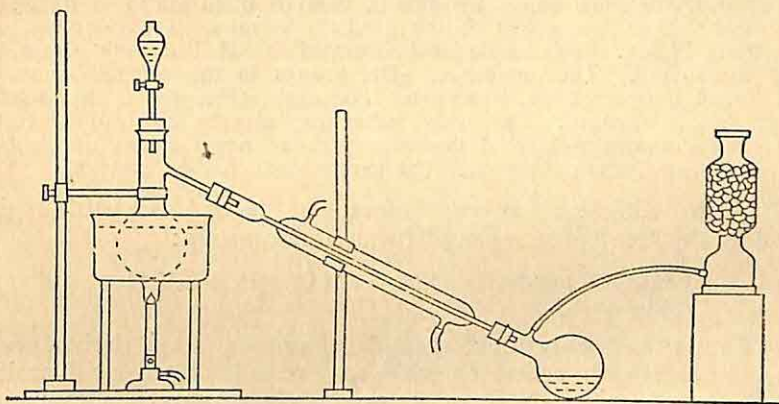
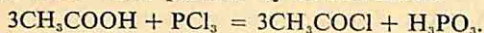


Fig. 32. Preparation of acetyl chloride.

A convenient laboratory method is to heat benzoyl chloride and acetic acid, the more volatile acetyl chloride distils off first; or to treat acetic anhydride with HCl at $85-90^\circ$.



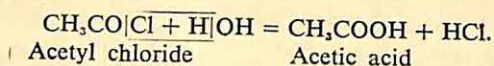
Commercially, it is made from sodium acetate and a mixture of sulphur dioxide and chlorine.



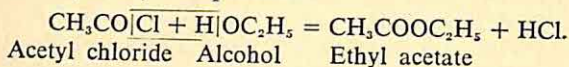
Properties.—Acetyl chloride and other lower acid chlorides are colourless, fuming liquids; the higher members are crystalline. They have an irritating odour, burn the skin and are readily decomposed by water. As a rule, they boil at a much lower temperature than the parent acids as they cannot associate by hydrogen bonding. They are readily halogenated in the α -position. The chlorine is highly reactive due to the inductive effect of doubly-linked oxygen (cf. much less active alkyl chlorides, $\text{R.CH}_2\text{Cl}$) which produces a lower electron density on

the carbon of the CO group, $R-\overset{+}{C}=\overset{-}{O}$, and facilitates reactions with nucleophilic agents.

Reactions.—(1) Water rapidly decomposes acetyl chloride to acetic acid at room temperature:

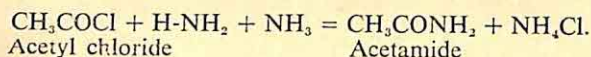


(2) Alcohols react with it to produce esters. In fact, acetyl chloride reacts with *all* hydroxy-compounds:

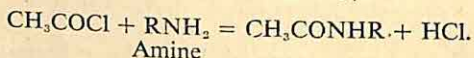


-O.CO.CH₃ is called acetoxyl group, and the process acetylation. Acetyl chloride is used for the detection and estimation of -OH group in organic compounds. The dry hydroxy-compound is heated under reflux with excess acetyl chloride for some time. Pyridine (a base) is often added to fix up the HCl formed. A known weight of the purified derivative is decomposed with fairly strong H₂SO₄. The acetic acid liberated is distilled with steam and titrated with alkali. The number of -OH groups in the original compound can be found if its mol. wt. is known. For each -OH group, one molecule of acetic acid is obtained. The acetyl value may also be obtained by boiling under reflux a known weight of the ester with a known excess of alcoholic potash until hydrolysis is complete. The excess alkali is then titrated.

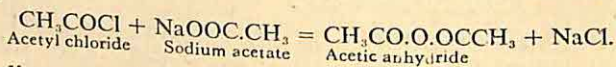
(3) With sufficient strong ammonia, acetyl chloride gives *acetamide*, chlorine being replaced by an amido group:



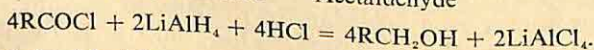
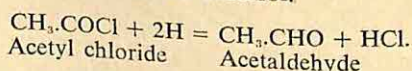
(4) Similarly, primary and secondary amines (alkyl derivatives of ammonia) react with acetyl chloride to give substituted acid amides. The number of amino, -NH₂, or imino, >NH, groups in a compound may be found in the same way as -OH groups.



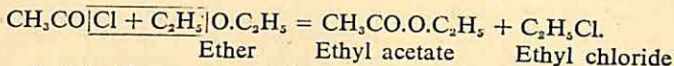
(5) Acetyl chloride, heated with fused sodium acetate, gives acetic anhydride.



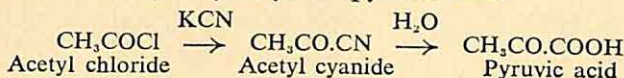
(6) Sodium amalgam and dilute acid, or hydrogen at 150° in presence of palladium reduces it to acetaldehyde. Further reduction to alcohol is prevented by 'poisoning' the catalyst with a little sulphur compound. Aldehydes are thus indirectly obtained from acids, direct reduction of acids being difficult. Lithium aluminium hydride in ether solution reduces an acyl halide to alcohol.



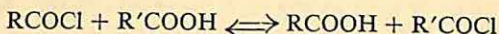
(7) Acetyl chloride reacts on heating with ether in presence of anhydrous ZnCl₂ and forms ethyl acetate and ethyl chloride:



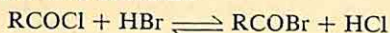
(8) Acetyl chloride reacts with potassium cyanide to give acetyl cyanide which, on hydrolysis, yields pyruvic acid:



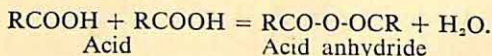
(9) Acid chlorides and carboxylic acids react to exchange their alkyl groups:



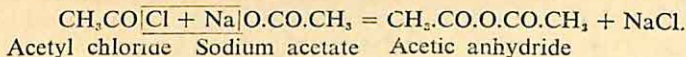
Acid bromides or iodides may be obtained from acid chlorides with excess of anhydrous HBr or HI. They closely resemble the acid chlorides, but boil at a higher temperature than the corresponding acid chlorides. They are more costly but no better than acid chlorides.



Acid anhydrides.—The anhydrides of monobasic organic acids may be regarded as derived from two molecules of the acid by the elimination of one molecule of water.



This is analogous to the formation of ethers from monohydric alcohols (p. 118). They may be called *acyl oxides* as ethers are regarded as alkyl oxides. They derive their names from the parent acid or acids by replacing 'acid' with 'anhydride.' The lower anhydrides cannot ordinarily be obtained from acids by abstraction of water with dehydrating agents like P_2O_5 . They are commonly prepared by heating the acid chloride with sodium salt of the acid:



By taking the sodium salt of one acid and the acid chloride of another, we get a *mixed* anhydride (cf., mixed ethers, p. 118) which are not quite stable: $\text{RCOCl} + \text{R}_1\text{COONa} = \text{RCO} \cdot \text{O} \cdot \text{COR}_1 + \text{NaCl}$. On standing, simple anhydrides result by interaction of two molecules. The acid chloride may be replaced by POCl_3 or SOCl_2 which acts on the fatty acid salt to give the acid chloride:



Anhydrides of higher fatty acids are made by heating the sodium salt of the acid with acetic anhydride, or by distilling the anhydrous acid with dehydrating agents such as phosphorus pentoxide or acetic anhydride.

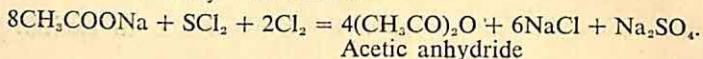


Formic anhydride does not exist; a mixed anhydride of formic and acetic acid, $\text{HCO} \cdot \text{O} \cdot \text{COCH}_3$, made from formic acid and acetic anhydride, is however, known.

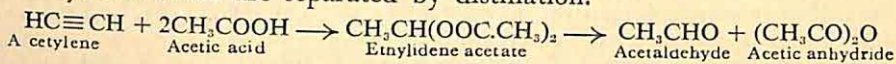
Preparation of acetic anhydride.—50 g. of powdered, fused sodium acetate are taken in a flask fitted with a separating funnel, a condenser and a receiver. 40 g. of acetyl chloride are slowly added, while the flask is kept cool with

water. When all the acetyl chloride has been added, the contents are thoroughly shaken and distilled. Acetic anhydride distils between 135° - 140° . Instead of acetyl chloride, cheaper POCl_3 or SOCl_2 may be employed. A small filtering flask is used as receiver, its side-tube being connected to a calcium chloride tube to arrest moisture.

Acetic anhydride is manufactured by mixing sodium acetate with sulphur dichloride, SCl_2 , and passing chlorine at 15° - 20° . The anhydride is obtained by distillation.



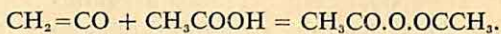
(2) U.S.A. makes it by passing acetylene at 60 - 85° into acetic acid containing HgSO_4 , ethylidene acetate formed is decomposed by heat in presence of ZnCl_2 catalyst or H_2SO_4 into acetaldehyde and acetic anhydride which are separated by distillation.



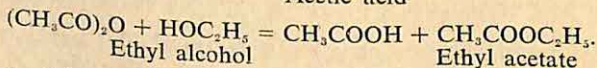
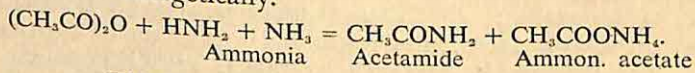
(3) Acetic anhydride may be prepared by passing glacial acetic acid vapour over zinc oxide or barium oxide at 250 - 300° .



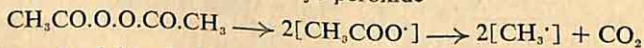
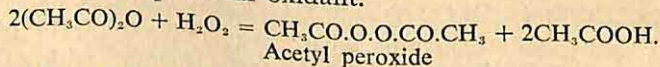
(4) It is also made by passing ketene (p. 136) into glacial acetic acid.



Properties.—Acetic anhydride is a colourless, neutral liquid (b.p. 137°) with a pungent odour resembling that of acetic acid, and has a density 1.082 at 20° . The anhydride is slightly soluble in cold water which slowly decomposes it to acetic acid. The aqueous solution may serve for acetylation. It is used for the detection and estimation of hydroxyl groups in organic compounds. Anhydrous sodium acetate, zinc chloride or strong H_2SO_4 accelerates acetylation. Ordinarily, tertiary alcohols are not thus acetylated; they can, therefore, be distinguished from the primary and the secondary. Acetic anhydride reacts with ammonia and hydroxy-compounds in the same way as acetyl chloride, but less energetically.



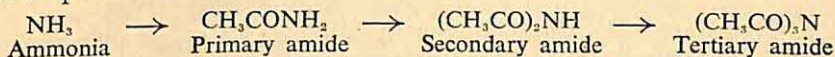
Acetic anhydride (or acetyl chloride) and alkaline H_2O_2 form acetyl peroxide which decomposes to give free acetate and methyl radicals. Acetyl peroxide is a powerful oxidant.



Acetic anhydride is largely used for making acetate rayon, some dyes and pharmaceuticals, e.g., aspirin. Other fatty acid anhydrides resemble acetic anhydride. The lower ones are more reactive. The

higher members are odourless solids. Their boiling points are higher, but melting points lower, than those of the corresponding acids. Acid anhydrides are reduced to alcohols by LiAlH_4 in ether solution.

Acid amides.—If the hydrogen of ammonia be replaced by alkyl radicals, the products, RNH_2 , etc., are called *alkyl amines*; but if substituted by acyl radicals, we get *acid amides*. These are primary, secondary or tertiary according as one, two or three hydrogen atoms of ammonia are replaced by acyl groups. Primary acid amides are the most important.



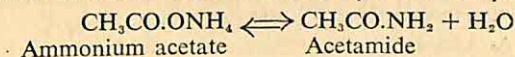
Amides may also be regarded as acids the -OH of which has been replaced by an amino group: $\text{RCOOH} \longrightarrow \text{RCONH}_2$. When -NH₂ replaces -OH in a -COOH, it is called an *amido group*. The amides are named by replacing *ic acid* of the parent acid by *amide*, e.g., formamide, HCONH_2 .

Formamide, HCONH_2 , is prepared by heating ammonium formate, HCOONH_4 , in an atmosphere of ammonia.

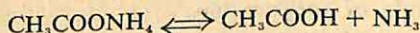


It is a hygroscopic, unstable liquid (b.p. 200°) readily soluble in water and alcohol. Formamide splits up into CO and NH_3 at its b.p. unlike other acid amides and is hydrolysed more easily. It is an ionising solvent like water or liquid ammonia, and has a high dielectric constant of 84. Formamide dissolves many organic compounds. HCN is made by dehydrating HCONH_2 .

Acetamide, CH_3CONH_2 , is conveniently made by slowly distilling ammonium acetate. It is a case of partial dehydration.



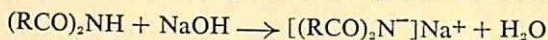
Preparation.—50 g. of ammonium acetate and 50 c.c. of glacial acetic acid are taken in a 250 c.c. round-bottomed flask, fitted with a long, upright glass tube. The mixture is gently boiled for about 4 hours. The water formed escapes and the reaction goes to completion. The contents are transferred, while still warm, to a distilling flask carrying a thermometer and an air condenser. The receiver is changed at 215° . The distillate solidifies to a colourless, crystalline mass. It is almost pure acetamide and may be further purified by recrystallisation from alcohol or benzene. Acetic acid retards the side-reaction:



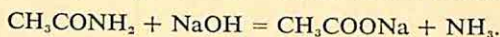
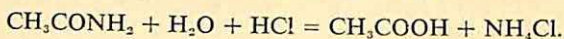
Properties.—Acetamide is a colourless, crystalline solid (m.p. 82° , b.p. 220°), highly soluble in water, alcohol or ether. Due to impurities, it has an odour of mice, but the product recrystallised from acetone is odourless. The amide is believed to be a dimer to account for its high b.p. The aqueous solution is neutral to litmus. The amino group has largely lost its basic character due to the proximity of the electron-attracting carbonyl group (cf., $\text{CH}_3\text{CH}_2\text{OH}$ which is neutral, giving acetic acid, $\text{CH}_3\text{CO.OH}$, p. 152). Acetamide is amphoteric ($K_A = 8.3 \times 10^{-16}$; $K_B = 3.1 \times 10^{-15}$); it forms unstable salts with strong acids, e.g., acetamide hydrochloride, $\text{CH}_3\text{CONH}_2 \cdot \text{HCl}$, and also gives

mercury acetamide, $\text{Hg}(\text{NH}.\text{CO}.\text{CH}_3)_2$, with HgO . It is a good solvent for many organic compounds.

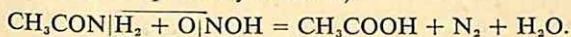
The replacement of a hydrogen atom of NH_3 by an acyl group, $\text{RCO}-$, which is electrophilic, reduces the capacity of nitrogen of the resulting amide to share its lone electron pair. Unlike ammonia, NH_3 , or amines, RNH_2 , amides, RCONH_2 , do not form salts that are stable in water. If two hydrogen atoms of NH_3 be replaced by acyl groups, their electron attracting effect is quite sufficient to allow the escape of the remaining hydrogen atom of the secondary amide as proton to strong bases in aqueous solution, e.g.,



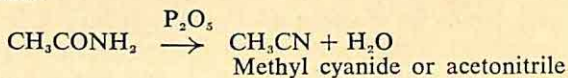
Reactions.—(1) On boiling with dilute acids or alkalis, acetamide is readily hydrolysed; alkalis are much more effective.



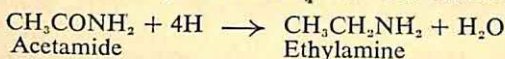
(2) Nitrous acid converts it to acetic acid, nitrogen being liberated (*cf.*, action of HNO_2 on primary amines).



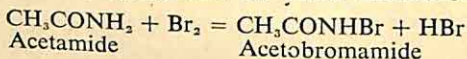
(3) On distilling amides with dehydrating agents *e.g.*, P_2O_5 , alkyl cyanides are obtained:



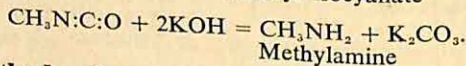
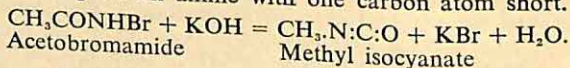
(4) Sodium and ethanol, or LiAlH_4 reduces amides to amines:



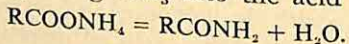
(5) Bromine acts on acetamide to yield acetobromamide.



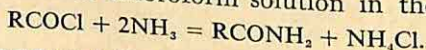
In presence of KOH , bromine converts the bromamide into isocyanate and finally, into methylamine. This is **Hofmann reaction** for preparing amines. An acid amide thus gives an amine with one carbon atom short.



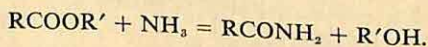
General methods of preparation.—(1) By distilling ammonium salts of fatty acids, or passing NH_3 into the acid at $150^\circ\text{--}200^\circ$.



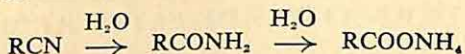
(2) By the action of dry ammonia upon acid chlorides or anhydrides in benzene or chloroform solution in the cold:



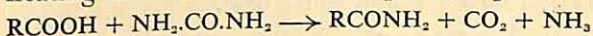
(3) By reaction of esters with an excess of conc. ammonia solution at room temperature:



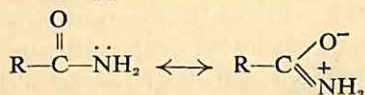
(4) By the *partial* hydrolysis of alkyl cyanides with H_2O_2 and NaOH , or moderately strong, cold H_2SO_4 ; complete hydrolysis yields ammonium salt of the acid.



(5) By heating an acid with urea, $\text{NH}_2\text{CO.NH}_2$.



General properties.—Acid amides except formamide are colourless, crystalline solids. Their boiling and melting points are much higher than those of the parent acids due to association through hydrogen bonding. The lower members are soluble in water, their aqueous solution is neutral to litmus. The higher members are less soluble and slightly basic in character, forming unstable salts with strong acids; the salts are hydrolysed readily. The hydrogen of the amido group can be replaced by some metals, *e.g.*, mercury and sodium, showing their weakly acid character. Amides are hydrolysed to the free acid and ammonia slowly by water, quickly by acids and much more quickly by alkalis. In chemical behaviour, they resemble acetamide. They are resistant to oxidation. Both formamide and acetamide are good solvents. Amides appear to be resonance hybrids:



QUESTIONS

1. How would you detect the presence of (a) a hydroxyl group, (b) unsaturation, (c) an aldehyde group and (d) nitrogen in organic compounds? Dacca Uni. B.Sc., Pass, 1933.

2. Describe with essential practical details, the preparation of acetyl chloride in the laboratory. What are its main properties and uses? Calcutta Uni. B.Sc., Pass, 1944.

3. How can you convert ammonium acetate and methyl cyanide into acetamide? What is the action of phosphorus pentoxide, boiling caustic alkali and moderately strong H_2SO_4 upon acetamide?

4. What are acid anhydrides? How do they differ from ethers? How would you obtain a pure specimen of acetic anhydride? What are its chief uses?

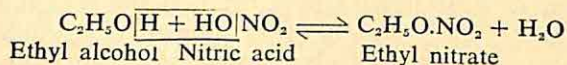
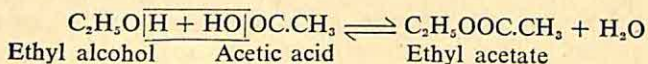
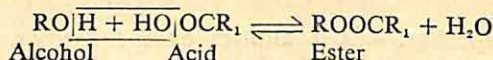
5. How does acetyl chloride react with (a) water, (b) ethyl alcohol, (c) ammonia, (d) sodium acetate and (e) caustic soda?

6. How could you convert acetyl chloride into (a) acetamide, (b) acetic acid and (c) acetic anhydride?

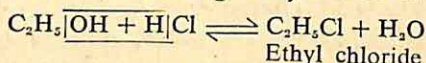
CHAPTER XV

THE DERIVATIVES OF FATTY ACIDS—II

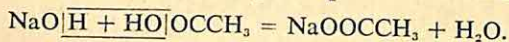
The esters.—When an alcohol reacts with an acid—organic or inorganic—we get an *ester* and water, *e.g.*,



Alkyl halides are esters of halogen hydracids and alcohols:



This superficially resembles the reaction between an acid and a base, giving salt and water. Hence the name alkyl salts for esters. But unlike esterification, the acid-base reaction is ionic, irreversible, and almost instantaneous at ordinary temperature without a catalyst.



Esters may as well be regarded as derivatives of acids obtained by replacing one or all the ionisable hydrogen by alkyl groups:

Acids	Esters
H_2SO_4	$\text{CH}_3 \cdot \text{HSO}_4$, $(\text{CH}_3)_2\text{SO}_4$
CH_3COOH	$\text{CH}_3\text{COOCH}_3$, $\text{CH}_3\text{COOC}_2\text{H}_5$, etc.
RCOOH	RCOOR_1

Esters, originally called 'ethereal salts', are named from the acid and the alkyl radical (of the alcohol)—the latter being mentioned first, *e.g.*, ethyl acetate, $\text{CH}_3\text{COOC}_2\text{H}_5$, ethyl hydrogen sulphate, $\text{C}_2\text{H}_5 \cdot \text{HSO}_4$, and so on. In the formation of organic esters, the acid, not the alcohol, supplies the $-\text{OH}$ of the water formed, but with a halogen acid *e.g.*, HCl , the reverse must be the case. Thus if the organic acid contains $-\text{O}_{16}\text{H}$ and the alcohol, the heavier, isotopic O_{18} , ordinary water results during esterification. Furthermore, acetic acid and ethyl mercaptan, $\text{C}_2\text{H}_5\text{SH}$, form ethyl thioacetate, $\text{CH}_3\text{COS} \cdot \text{C}_2\text{H}_5$, and water. The rates of esterification with organic and inorganic acids are also different.

Isomerism.—(i) There may be isomerism in the alkyl radical of the acid or the alcohol, *e.g.*, (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOC}_2\text{H}_5$, ethyl butyrate, and $(\text{CH}_3)_2\text{CHCOOC}_2\text{H}_5$, ethyl isobutyrate; (b) $\text{CH}_3\text{COOCH}(\text{CH}_3)_2$, isopropyl acetate, and $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}_3$, propyl acetate.

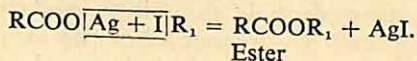
(ii) The alkyl group of the acid and the alcohol may be both different. Thus $\text{C}_2\text{H}_5\text{O}_2$ represents methyl butyrate, $\text{C}_3\text{H}_7\text{COOCH}_3$, ethyl propionate, $\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5$, propyl acetate $\text{CH}_3\text{COOC}_3\text{H}_7$, and butyl formate, HCOOC_4H_9 . The isomeric esters in (i) and (ii) may be distinguished by hydrolysis.

with moderately strong sodium carbonate solution to neutralise the acids. The lower aqueous layer is drawn off and the upper oily layer of the ester is treated with a strong solution of NaCl or CaCl_2 to remove the alcohol. The ester is dehydrated with fused CaCl_2 and purified by re-distillation from water-bath. The liquid coming between 75° and 80° is collected. By taking an excess of the alcohol, the yield of ester is increased to 80-88% of the theoretical.

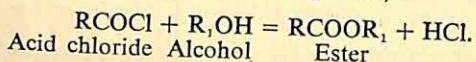
Alternatively, dry HCl gas is passed into alcohol until weight increases by about 20%. This is added to an equal volume of glacial acetic acid, taken in a flask, fitted with a reflux condenser. The flask is heated on water-bath for about half-an-hour. The contents of the flask are poured into strong brine and the upper layer of the ester separated. It is purified as before. This method is quicker, a large excess of alcohol is also unnecessary. No ether is formed as with H_2SO_4 .

Ethyl acetate is a colourless, sweet-smelling liquid (b.p. 77.5° and sp. gr. 0.91), slightly soluble in water. It may be made from acetaldehyde (p. 132). It is a solvent for lacquers.

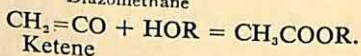
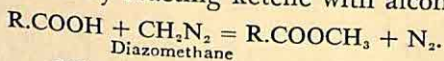
(2) By boiling an alkyl iodide with dry silver salt of fatty acids, esters are formed (cf. Williamson's synthesis of ether, p. 120). Esters of unstable or very weak acids can thus be prepared. The method is costly and also slow.



(3) On warming acid chlorides with alcohols, esters are obtained readily in good yield (p. 162). The mixture is shaken with dilute caustic soda solution to remove the hydrochloric acid. Anhydrides also react with alcohols to give esters (p. 164).

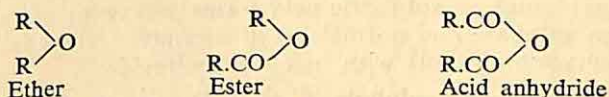


(4) Methyl esters may be made by treating the acid with an ethereal solution of diazomethane (a yellow gas) at room temperature, and esters of acetic acid by reacting ketene with alcohols:

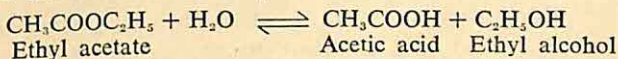


Properties and uses.—Esters are colourless, neutral liquids or solids, with fragrant odour, resembling that of fruits in many cases. Many occur in essential oils of plants; they are widely used as artificial flavouring essences and in perfumery. Ethyl butyrate has the odour of pineapple, isoamyl isovalerate that of apple. Esters are mostly lighter than water in which they are but sparingly soluble. They are soluble in alcohol and ether. Methyl and ethyl esters of fatty acids boil at much lower temperatures than the acids because they cannot associate by hydrogen bonding. Methyl esters have invariably *higher* melting points than the corresponding ethyl esters. Some are excellent solvents; ethyl, butyl and amyl acetate are largely employed for dissolving collodion, celluloid, etc. Ethyl acetate (*acetic ether*), is a good stimulant. Ethyl formate is a fungicide; cellulose acetate, polymethyl

methacrylate and polyvinyl acetate are common plastics. Some are plasticizers (softening agents). Esters occupy an intermediate position between ethers and acid anhydrides—being more reactive than the former but less so than the latter. Their structural relationship explains this fact:

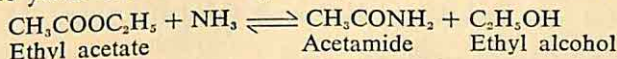


Reactions.—(1) Esters are slowly decomposed by boiling water to the parent alcohol and acid. The process is called *hydrolysis*. Ethyl acetate gives acetic acid and ethyl alcohol:



Mineral acids and alkalis accelerate this reaction. The acid hydrolysis is reversible, but the alkali fixes up the acid formed, and the opposite reaction cannot take place (*cf.* formation of soaps from natural oils and fats with caustic soda, p. 112). Esters are estimated by hydrolysis with standard alcoholic KOH and back titration of the excess alkali with standard acid.

(2) With ammonia gas or conc. aqueous or alcoholic ammonia, organic esters yield acid amides (p. 166). This is called *ammonolysis*.



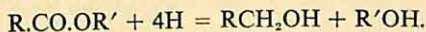
Esters of halogen hydracids (or alkyl halides) react with alcoholic ammonia and yield amines:



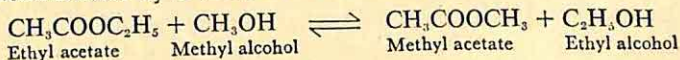
(3) Esters are converted into acid chlorides and alkyl chlorides by phosphorus pentachloride.



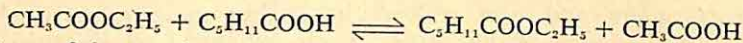
(4) On vigorous reduction, an ester gives *two* mols. of alcohol; *Bouveault-Blanc method* consists in refluxing an ester (or an aldehyde or a ketone) with excess sodium and absolute alcohol. Free fatty acids are not so readily reduced. Lithium aluminium hydride, LiAlH_4 , reduces esters (and also acids, aldehydes, ketones, etc.) in ether solutions to alcohols in very good yield; it does not normally reduce an olefinic bond. Sodium hydride, NaH , gives a higher yield of alcohol from ester than sodium and alcohol. Catalytic, high pressure hydrogenation also effects reduction; lauryl alcohol, $\text{C}_{12}\text{H}_{25}\text{OH}$, is thus commercially made from cocoanut oil.



(5) When ethyl acetate is refluxed with a large excess of methyl alcohol, methyl acetate is formed. Similar reversibility also occurs with other esters; this is known as *alcoholysis* (splitting by alcohol). The process is accelerated by a little acid or alkali.

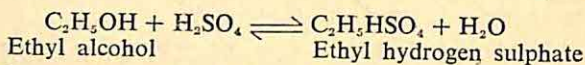


In acidolysis, the acid residue of an ester can be similarly replaced by another:



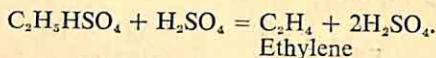
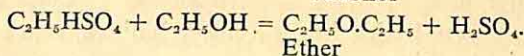
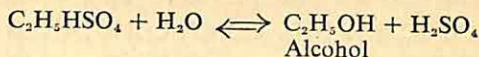
Esters of inorganic acids are prepared like organic esters. A dibasic acid such as sulphuric acid forms two types of esters, *viz.*, alkyl hydrogen sulphate and normal alkyl sulphate. Alkyl halides are esters of monohydric alcohols with halogen hydracids.

Ethyl hydrogen sulphate, $\text{C}_2\text{H}_5\text{HSO}_4$, is prepared by heating on water-bath, equal volumes of ethyl alcohol and conc. H_2SO_4 , for about an hour.

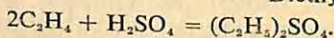
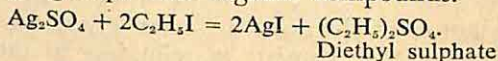


The liquid is treated with sufficient BaCO_3 , excess of H_2SO_4 is precipitated as BaSO_4 and filtered off. The barium salt of ethyl hydrogen sulphate remains in solution. It is decomposed by just sufficient dilute H_2SO_4 in the cold and filtered. The filtrate is distilled under reduced pressure, alcohol and water are thus removed and ethyl hydrogen sulphate is obtained as a thick liquid.

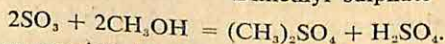
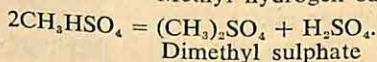
Ethyl hydrogen sulphate (formerly called sulphovinic acid) is sour to the taste and like bisulphates has an acid reaction, decomposing carbonates. It is readily decomposed by boiling water, alcohol or sulphuric acid.



Diethyl sulphate is best prepared by heating silver sulphate with ethyl iodide and industrially, by passing excess of ethylene into cold, concentrated sulphuric acid. It is a colourless liquid (b.p. 208°), used for introducing ethyl groups into organic compounds.



Dimethyl sulphate, $(\text{CH}_3)_2\text{SO}_4$, is made by the action of chlorosulphonic acid, SO_3HCl , on methyl alcohol below 0° and distilling the product under reduced pressure, or by treating methanol with SO_3 at low temperature.



A German process consists in passing dimethyl ether and SO_3 in molar ratio into dimethyl sulphate at 40° and distilling the product with Na_2SO_4 at low pressure.

Dimethyl sulphate is a heavy, odourless liquid (b.p. 188°) *highly poisonous*. It is slowly hydrolysed by water even in the cold. It reacts

with compounds having -NH_2 , -OH or >NH groups in presence of alkalis, replacing the hydrogen atoms by methyl groups, hence its use for methylation.

In recent years, a new class of detergents (cleansing agents) in the form of sulphates of higher fatty alcohols, has been developed. Unlike ordinary soaps, these can be used in hard water—their Ca and Mg salts being soluble. These are more soluble in water, have a greater spreading or penetrating power and can be used in acid or alkaline medium. Some 40% of the domestic and industrial detergents are now of this kind. Like soaps they have an electrovalent or polar group (-COOH , $\text{-SO}_3\text{H}$ or $\text{-OSO}_3\text{H}$) and a covalent or non-polar group (alkyl group or alkyl-substituted benzene ring). The former attracts water and the latter oils, so that oil and water come together and form a stable emulsion. Cetyl sodium sulphate, $\text{C}_{16}\text{H}_{33}\text{O}_2\text{SO}_3\text{Na}$, is a detergent of this group; sodium lauryl sulphate, $\text{C}_{12}\text{H}_{25}\text{O}_2\text{SO}_3\text{Na}$, is a good wetting agent and a detergent. Higher fatty acids form the corresponding primary alcohols when their esters (e.g. glycerides) are reduced with H_2 under pressure using a Ni catalyst; these alcohols are sulphated with fuming H_2SO_4 .

Ethyl nitrate, $\text{C}_2\text{H}_5\text{NO}_3$.—Nitric acid and ethyl alcohol produce ethyl nitrate, but alcohol is oxidised by nitric acid. The resulting nitrous acid with alcohol forms ethyl nitrite. The yield of ethyl nitrate is thus poor even at low temperature. Urea, $\text{CO}(\text{NH}_2)_2$, decomposes the nitrous acid as it is formed and improves the yield.



The reaction mixture is *very slowly* distilled from water-bath otherwise ethyl nitrate may explode. Ethyl nitrate is a liquid (b.p. 86°) with a fruity smell, insoluble in, and heavier than, water. Tin and HCl reduce it to alcohol and hydroxylamine, NH_2OH .

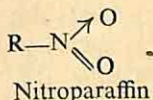
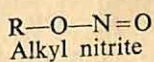


Ethyl nitrite, $\text{C}_2\text{H}_5\text{O.NO}$, is prepared by treating *in the cold* a mixture of potassium nitrite and alcohol with dilute HCl or H_2SO_4 . It is purified by distillation from warm water-bath, and condensed in a receiver cooled with ice. It may be dried over pot. carbonate. The ester (b.p. 16°) has the odour of apples.

Sweet spirit of nitre, a stimulant, is made by the action of H_2SO_4 , HNO_3 and copper upon ethyl alcohol. It contains besides alcohol and ethyl nitrite, some acetic acid, ethyl acetate, etc.

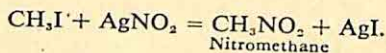
Amyl nitrite, $\text{C}_5\text{H}_{11}\text{O.NO}$, prepared like ethyl nitrite, is a pale yellow liquid (b.p. 96°), used as a heart-stimulant. Iso-amyl nitrite (b.p. 99°) relieves spasms of arteries in asthma by reducing blood pressure.

Nitroparaffins, R.NO_2 , are isomeric with alkyl nitrites and may be regarded as derived from paraffins by replacing a hydrogen with a nitro-group, -NO_2 .

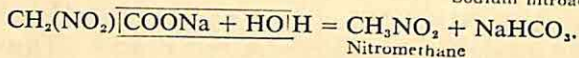
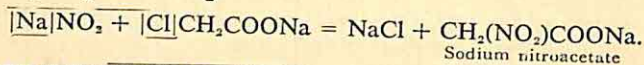


Paraffins from hexane upwards can be directly nitrated with fuming nitric acid, but not the lower members. Propane and nitric acid, however, react in vapour phase at $400\text{--}500^\circ$ and yield nitromethane, nitroethane, 1-nitropropane and 2-nitropropane, which may be separated by fractional distillation. These are good solvents for cellulose acetate and vinylites, and made commercially. Ethane thus gives nitro-ethane

and nitromethane. Lower nitroparaffins are usually prepared by distilling an alkyl iodide with solid silver nitrite; some alkyl nitrite is also formed.



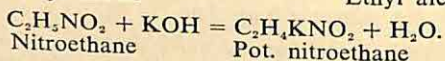
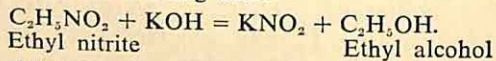
Victor Meyer, who discovered the nitroparaffins in 1872, obtained a mixture of ethyl nitrite and nitroethane by reacting ethyl iodide with silver nitrite. Both nitromethane (b.p. 101°) and nitroethane (b.p. 114°) are pleasant-smelling, colourless, inflammable liquids, insoluble in water. Nitromethane may be easily prepared in good yield by heating equimolecular amounts of sodium nitrite and sodium monochloroacetate in aqueous solution. Nitroacetic acid, first formed, breaks up into CH_3NO_2 and CO_2 :



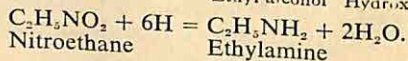
With other metallic nitrites, except AgNO_2 , alkyl nitrite results and no nitroparaffin. Again, with AgNO_2 , methyl iodide produces only nitromethane, whereas ethyl iodide gives almost equal quantities of nitroethane and ethyl nitrite. With higher alkyl iodides increasingly higher amounts of ester result. Nitroparaffins, as a rule, have much higher boiling points than isomeric alkyl nitrites; they are easily separated by fractional distillation. **Tetranitromethane**, $(\text{NO}_2)_4\text{C}$, made from acetic anhydride and fuming HNO_3 , gives, in chloroform solution, a yellow to red colour with unsaturated compounds; a very dilute solution in the cold is employed for their test as it explodes violently on heating with organic compounds.

Distinction between alkyl nitrites and nitroparaffins.—(i) A nitroparaffin boils at a much higher temperature than the corresponding alkyl nitrite.

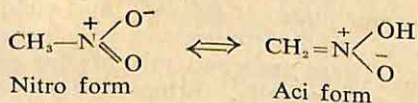
(ii) Alkyl nitrites are hydrolysed to alcohol by caustic alkali but nitroparaffins dissolve in the alkali forming salts.



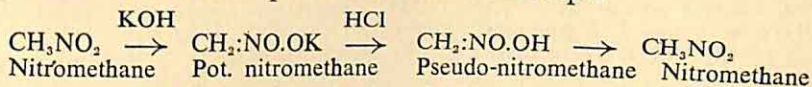
(iii) Alkyl nitrites, on reduction, give alcohol and nitrous acid which is further reduced to hydroxylamine or ammonia. But powerful reducing agents, e.g., tin and HCl , convert nitroparaffins to primary amines.



These reactions show that the nitrogen of nitroparaffins cannot be easily detached. It is, therefore, believed to be directly linked to carbon. To explain reactions (ii) and (iii), a nitroparaffin (primary or secondary) is supposed to exist in two tautomeric forms (hydrogen bonding between molecules of aci-form possibly explains the high boiling point of nitroparaffins):



The nitro form is reduced to amine while the aci form gives salt with alkali. It has been possible to follow the steps:



Compounds like nitromethane, which are neutral but form acids by intramolecular change, are known as *pseudo-acids*. Tertiary nitro-paraffins have no H with the C adjacent to N; they cannot be tautomeric and are not soluble in alkali.

Victor Meyer's method for distinguishing between primary, secondary and tertiary alcohols by converting them into the corresponding nitroparaffins (p. 95) may be recalled. With HNO_3 , primary nitroparaffins give nitrolic acids, the secondary form pseudo-nitrols while the tertiary do not react at all.

Oils, fats and waxes.—In nature, we meet with three types of oily substances : (i) **Fixed fats and oils**, animal or vegetable, are glycerides of higher fatty acids (p. 155), usually containing an even number of carbon atoms, such as oleic, stearic and palmitic acid. They are non-volatile, mixed triglycerides (p. 112). Fats are harder in consistency. Glycerides melting above 20° are usually termed fats while oils melt below 20°. In India, cocoanut oil in summer may become a fat in winter. (ii) **Mineral oils**, mixture of hydrocarbons, are of mineral origin as the name indicates ; e.g., kerosene oil, diesel oil. (iii) **Essential oils** are highly volatile, pleasant-smelling liquids found in various plants ; clove oil, lemon oil, turpentine, etc. are examples. Their compositions differ ; they are usually aromatic or alicyclic.

Waxes are solid esters of higher monohydric alcohols with higher fatty acids, resembling fats. Any solid with a waxy feel and melting between 37° and 100°, is commonly termed wax. Paraffin wax is a mixture of hydrocarbons (p. 51). Bees-wax (m.p. 60-82°) is chiefly myricyl palmitate, $C_{15}H_{31}COOC_{30}H_{61}$. Spermaceti (m.p. 42-50°), secreted by the sperm-whale, is mainly cetyl palmitate, $C_{15}H_{31}COO.C_{18}H_{37}$; it is used in pharmacy and in making candles. Carnauba wax (m.p. 80-87°), found in carnauba palm leaves in Brazil, is largely employed in making gramophone records, furniture and boot polish. It is the myricyl ester of cerotic acid, $C_{22}H_{43}COOC_{30}H_{61}$. Wool wax is mostly cholesterol ester of cerotic acid. In lead pencils, wax is a binder for graphite, silica, etc. ($C_{27}H_{45}OH$) esters. In lead pencils, wax is a binder for graphite, silica, etc. Carbon paper, cosmetics, some lubricants and polishes contain wax. Oils, fats and waxes are commonly called **lipids**.

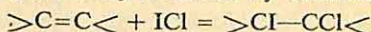
Vegetable oils usually occur in seeds. Crushed seeds are packed in linen bags and subjected to a high pressure in hydraulic press; if necessary, the temperature is raised. The oil exudes leaving residual 'oil-cake', a cattle food. The extraction is also done with solvents like carbon tetrachloride, benzene, etc., the solvent is recovered and used again; the process is rather costly though very effective. Animal oils are obtained from the fatty tissues, kidneys, livers, etc. which are chopped and boiled with water or live steam, the melted fat floats on the surface and is separated. Crude oil is purified by adding a little alkali to remove free acids, bleached with plaster of Paris, charcoal or fuller's earth at 70-80°, and finally deodorised with steam.

Properties.—Natural oils and fats are neutral, lighter than water and readily soluble in benzene, acetone, ether, carbon tetrachloride, etc. Glycerides of saturated fatty acids are mostly solids while those of unsaturated acids are liquids. The consistency is largely determined by the proportion of unsaturated glycerides. Oils are partially decomposed when boiled under atmospheric pressure, irritating vapour of acrolein is evolved. Some glycerides of unsaturated acids (e.g., linseed oil) slowly absorb oxygen from the air and form a hard, transparent mass due to oxidation and polymerisation. They are known as *drying oils*. But unsaturation alone does not always determine the drying property as fish-oils having glycerides of highly unsaturated fatty acids do not dry in air.

On exposure to light, air and moisture, oils slowly become rancid due to the formation of peroxides by unsaturated glycerides, which split up into aldehydes, ketones and acids. Some of these have strong odour and rancid taste. Anti-oxidants e.g., hydroquinone, inhibit this reaction. The odour of a fresh oil is mostly due to impurities, e.g., allyl isothiocyanate, C_3H_5NCS , in mustard oil.

Hydrogenation of oils.—In recent years, the process of converting liquid oils into fats by adding hydrogen to the double bond in the unsaturated glycerides, has been industrially developed. This hardening or hydrogenation of oils is carried out with pure hydrogen under pressure (60 lb.) in presence of finely divided nickel (obtained by heating nickel formate in oil at 240° ; 0.2–0.5% on the weight of oil added) at 120 – 176° . The oil and catalyst are agitated violently in a closed vessel and hydrogen bubbled in. The nickel is filtered off and used again. *Vegetable ghee* or *vanaspati* is hydrogenated oil. Hardened oils are extensively used for the manufacture of margarine (a butter substitute, made by thoroughly mixing fats, oils, hydrogenated oils and milk, and adding vitamins and colouring matter to the mixture), soap and candle. India produced 2,95,154 tons of vanaspati in 1958, mostly from groundnut oil.

Analysis of oils.—(i) **Iodine value** indicates the unsaturated nature of an oil. Iodine chloride, ICl , is readily absorbed by unsaturated glycerides:



A known excess of ICl solution is added to a definite weight of oil dissolved in a solvent. Excess of ICl is estimated after absorption is complete. The amount of ICl absorbed is thus known (Wijs' method). Iodine value is the number of grams of iodine which thus combines with 100 g. fat or oil. The greater the iodine value, the greater evidently the unsaturation. Coconut oil has an iodine value of about 10, olive oil 88, and linseed oil 170–200. No fat or oil has zero iodine value.

(ii) **Saponification value** is the amount of caustic alkali, in mg. KOH , required to neutralise the fatty acids derived from 1 g. of fat or oil. A known weight of oil is heated under reflux with sufficient standard alcoholic potash, the excess is titrated with acid. Coconut oil has a saponification value of about 250, olive oil about 200. The higher the saponification value, the lower the average mol. wt. of constituent fatty acids and vice versa.

(iii) **Reichert-Meissl value** denotes the volume in c.c. of decinormal potash, required to neutralise the volatile acids obtained by the distillation of 5 g. of oil under specified conditions. Butter has a Reichert-Meissl value of about 28, coconut oil about 8, and lard 0.0.

On the basis of iodine value, oils are subdivided into three groups—drying, semi-drying and non-drying. Non-drying oils, having iodine values below 90, do not appreciably change their consistency on exposure to air. They chiefly consist of triolein, e.g., olive oil, coconut oil, castor oil, etc. *Drying oils*, with iodine values above 120, slowly harden to a resinous solid on exposure to air. They are mainly composed of highly unsaturated acids, such as linoleic, linolenic, etc. Linseed oil is the best example; it contains about 80 p.c. linolenic acid ester, 15 p.c. linoleic ester and 5 p.c. triolein. Drying oils are used in paints, in making oil-cloth, rexine, linoleum, etc. *Linoleum* is made by mixing ground cork with boiled linseed oil, rolling the resulting mass into sheets, and allowing them to harden. India is third in the production of linseed. Tung oil (China-wood oil) is an excellent drying oil. Semi-drying oils have iodine values between 90–120 and thicken very slowly in air; examples are cotton seed oil, sesame oil, etc. *Castor oil* contains the glyceride of ricinoleic acid or hydroxy-oleic acid. It is a lubricant and a purgative. Sulphonated castor oil is *Turkey Red oil*, a wetting agent in the textile industry.

Synthetic fats.—By heating paraffin wax with Na_2CO_3 solution under pressure at about 170° and passing air, a series of fatty acids—all with odd number of carbon atoms (C_{13} to C_{19}), are obtained. Lead, manganese or

vanadium is the catalyst. This process was developed in Germany during the war of 1914-18 to meet the demand of fatty acids when her oil seed supply was cut off. Glycerol was made by fermentation (p. 113).

Fats have been synthesised by heating glycerine with fatty acids in sealed tubes at 200°-260°. Mono-, di- and tri-glycerides are thus obtained. Oil seeds being abundant, synthetic fat has little prospect. During the war of 1914-18, Germany recovered fats from sewage of large cities, 3-4 kg. of fat is lost in faeces per head per annum. During the last war Germany oxidised hydrocarbons from Fischer-Tropsch process to acids and made fats and soaps therefrom.

Animal fats contain cholesterol, $C_{27}H_{46}O$, an unsaturated aromatic alcohol, which forms rhombic plates (m.p. 148°) while phytosterol (not a single body) occurs in vegetable oils, crystallising in needles (m.p. 132°-144°). A distinction is thus possible. Fats are formed in the animal body from carbohydrates, and stored as reserve food. During fast or muscular work, fats supply the energy. Lipase of the pancreas splits the fat we eat into glycerol and acids; fresh fat is built up therefrom in our system; the composition of human fat differs from that of fats we take. We derive about 9.5 kcal. of energy per gram of fat compared to about 4 kcal. per gram for protein or carbohydrate.

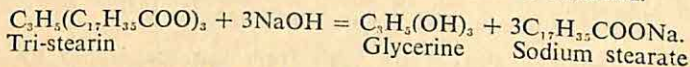
Hydrolysis of oils and fats (saponification).—(i) By heating under pressure the fat with water and 2-3% lime, magnesia or zinc oxide at 140-150°.

(ii) The fat-hydrolysing enzyme, lipase of castor seed, acts between 30°-40° on an emulsion of fat with very dilute sulphuric acid for 2-3 days and gives free acids.

(iii) With conc. H_2SO_4 (used only for poor qualities of fat).

(iv) With fatty-aromatic sulphonic acid (known as Twitchell's reagent) at about 100°. It acts rapidly on an emulsion of fat in water and a little H_2SO_4 .

Manufacture of soap.—Ordinary soap consists of sodium or potassium salts of higher fatty acids; these are soluble in water. The sodium salt gives hard soap, soft soap is the potassium salt; washing or toilet soap is usually hard soap. Soap is made from a mixture of fat and oil, the kind and proportion are trade secrets as the quality of soap largely depends on this choice. Cocoanut oil is used for ready lathering, and tallow or lard for permanence of lather. Palm oil, olive oil, cotton seed oil and other vegetable oils are extensively employed. For washing soaps, lard and cocoanut oil mixture is rather common. The mixture of melted, and in some cases, purified fats is boiled with live steam in large iron pans with the requisite amount of caustic soda solution (10%) called lye. The lye is slowly added, the steam agitates the mass and ensures thorough mixing. After several hours, a frothy mixture of sodium salts of the fatty acids, glycerine and water is obtained.



Common salt or brine is added, sodium salts of fatty acids separate at the surface as a granular mass after some hours. The process is called 'salting out'. Potassium soaps cannot thus be separated as they are decomposed by NaCl. The mother-liquor (called spent lye) contains glycerol; it is run off and worked for glycerine. The separated soap, having in it a little free fat, is again boiled with caustic soda to complete saponification. The lye is drawn off, the soap boiled with water and allowed to settle. The solid soap is then cut into chips, dried to the requisite moisture content, and mixed with perfumes and colouring matter. Finally, it is moulded into cakes in a dice. About 10% of rosin is often added to the fat charge to increase the solubility of the soap and give it a pleasant odour. The chief constituent of rosin is abietic acid, $C_{19}H_{33}COOH$, an aromatic compound.

In the cold process, tallow mixed with cocoanut oil is treated with the requisite quantity of warm NaOH solution (30%). Saponification takes place readily with liberation of heat. After adding perfumes, colouring matter, etc. the mass is allowed to set. The glycerine remains in the soap.

In a recently developed continuous process, a mixture of fats and oils and catalyst is forced up a vertical tower down which passes hot water. The glycerides are thus hydrolysed—the resulting fatty acids going to the top and glycerine, to the bottom of the tower. The acids are converted into soap with NaOH, and the glycerine recovered from its aqueous solution as usual.

Transparent soaps are made by dissolving ordinary soap in alcohol (methylated spirit) and driving off the alcohol after filtration. The mass on solidification looks transparent. Cold process soap, on adding cane-sugar and alcohol, becomes transparent. Floating soaps are made by blowing air through molten soap. For cheap toilet soaps as well as washing soaps, fillers such as soap-stone or magnesium silicate, sodium silicate, etc., are added in very fine form to increase the bulk. These soaps contain more moisture. High class toilet soaps should have not more than 10% moisture and no free alkali or fat. Rosin improves the detergent properties. Shaving sticks are potassium-sodium soaps made from tallow or lard; stearates produce a lasting lather, a desirable quality. Shaving soaps may contain gum or glycerine to prevent rapid drying of lather. Marine soaps, made from cocoanut and palm oil, lather with sea water. Liquid soap is a potassium soap dissolved in water.

Free fatty acids are also neutralised with sodium carbonate to form soaps. This is cheaper and simpler. Insoluble soaps are commercially important; lead soap (lead oleate) is a plaster in medicine; calcium and manganese soaps are lubricants, and also used as driers in paints. Zinc or magnesium stearate and palmitate are employed in face powders and ointments; aluminium soap makes textiles and leather water-proof.

The cleansing action of soap largely depends upon its wetting action as well as power of emulsification (due to polar and non-polar end-groups) and adsorption of grease and dirt particles. The dirt is mechanically removed during washing. Low surface tension of soap solution aids emulsification of greasy matter; electrostatic forces possibly play an important role.

Indian soap industry.—According to Liebig, consumption of soap is a measure of civilisation. In 1958 India produced 1,22,856 tons of soap. But the industry has to face hard competition with big foreign firms which have established factories here to avoid import duties. India's partial dependence for caustic soda and perfumes on foreign supply is a handicap. It is interesting to note that soap-making was known to the people of ancient India; Chakrapani (ca 1060 A.D.) gives a recipe for the preparation of a depilatory soap from mustard oil, ashes of certain plants, lime and the urine of the ass (Hindu Chemistry, by Sir P. C. Ray, Vol. I). Commercial production of soap appears to date from 1791 in Europe.

The annual consumption of soap per capita is 25 lb. in U.S.A., 20 lb. in Great Britain and only 4 oz. in India, a tropical country. Barely 5% of Indians use soap, no doubt, due to our appalling poverty.

Manufacture of candles.—Fatty acids from fats are refined by distillation with superheated steam at about 300°. The mixture of acids is heated to 60° and pressed to separate liquid acids. A solid cake, consisting chiefly of stearic and palmitic acids, is obtained. It is known as 'stearine', and mixed with suitable proportion of paraffin wax (about 90%) forms candles. Stearine makes the candles stronger. The mixture of melted stearine and paraffin is led into metal tubes carrying a pleated cotton thread along the axis. Finally it is obtained in the cylindrical form. Stearine candles are made in Burma, at Digboi, Calcutta, Madras, Mysore and Baroda.

Petrol from vegetable oils.—China makes petrol by cracking tung oil (a vegetable oil she has in abundance). This has gone a long way in solving her petrol problem.

QUESTIONS

1. How would you distinguish between (i) an aldehyde and a ketone, (ii) an ether and an ester, (iii) a nitroparaffin and an alkyl nitrite?—Dacca Uni., B.Sc., (Agri.), 1941.

2. How is ethyl acetate prepared in the laboratory? What is the action of (i) caustic soda, (ii) ammonia, on ethyl acetate?

3. How is soap manufactured? What are the essential qualities desired in a good toilet soap? Discuss the prospect of soap industry in India.

4. What is an ester? Write a short account of some of the more important members of this group of substances including those which have industrial value. Mention the general principles to be observed in the preparation of these compounds, and the nature and properties of the esters as a class. B.Sc., Pass, 1944, Calcutta Univ

5. What are oils and fats? How would you distinguish between an animal fat and a vegetable one? What are the commercial uses of oils and fats? How is candle manufactured?

6. Write what you know about isomerism of esters. How could you distinguish between the esters of the formula $C_4H_8O_2$?

7. Describe the preparation and properties of ethyl nitrite.—Calcutta Univ., B.Sc., Pass, 1934.

8. What is the chemical nature of a fat? How does it differ from an oil? Give an account of the principal methods of hydrolysis of oils and fats. B.Sc., Pass, 1930, Calcutta Univ.

9. How are oils hydrogenated? Discuss the economic aspects of such hardening of oils.

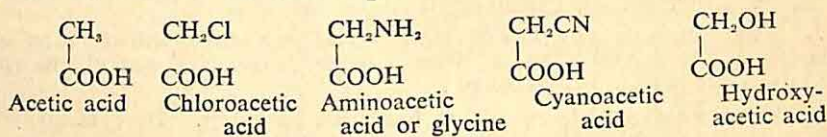
10. Mention the usual chemical tests by which the quality of an oil or fat may be determined. What is the mol. wt. of a fat whose saponification value is 200?

11. What are soaps? Describe how you would prepare a sample of soap by the cold process. How is glycerine recovered as a bye-product in the manufacture of boiled soaps?—B.A. Degree Exam., 1942, Madras Univ.

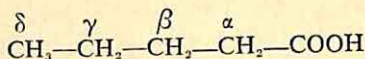
CHAPTER XVI

THE DERIVATIVES OF FATTY ACIDS—III

The halogen-, amino- and cyano-acids.—On replacing the hydrogen in the alkyl radical of fatty acids by other atoms or groups such as Cl, $-NH_2$, $-CN$, $-OH$, etc., various substituted acids are obtained. Acetic acid forms the following derivatives:



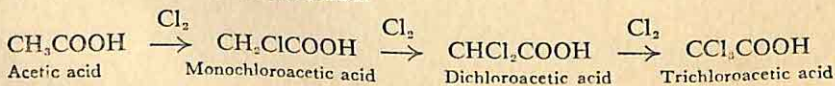
They exhibit more or less the properties of both the functional groups. Thus monochloroacetic acid behaves as an alkyl halide as well as an acid; hydroxyacids as alcohol and acid, and so on. Their properties may, however, be considerably modified by substituents. Thus monochloroacetic acid is much stronger, and aminoacetic acid weaker, than acetic acid. Only one monochloroacetic acid is known but there are two monochloropropionic acids, *viz.*, CH_2ClCH_2COOH and $CH_3CHClCOOH$. With higher homologues, the number of such isomers rapidly increases. More than one of the alkyl hydrogen atoms may, of course, be replaced by other atoms or groups. For convenience of nomenclature, carbon atoms of fatty acids are named with Greek letters. The one attached to the carboxyl group is termed α -, the next one β -, and so on; *e.g.*,



The three monochlorobutyric acids are accordingly named as $CH_2Cl-CH_2-CH_2COOH$, $CH_3CHCl-CH_2COOH$, $CH_3CH_2-CHClCOOH$
 γ -chlorobutyric acid β -chlorobutyric acid α -chlorobutyric acid

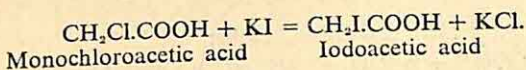
Halogen-substituted acids.—These are prepared by different methods depending upon the position the halogen takes. Chloroformic acid, $ClCOOH$, is unstable and known only as esters. The chloroacetic acids are commercially important.

Preparation.—(1) Chlorine or bromine is added to a boiling fatty acid in presence of a halogen carrier such as iodine, sulphur or phosphorus to get chloro- or bromo-acids. Hydrochloric or hydrobromic acid is evolved at each stage. The hydrogen atoms can be successively substituted. Sunlight promotes the reaction. Monochloroacetic acid is thus manufactured.

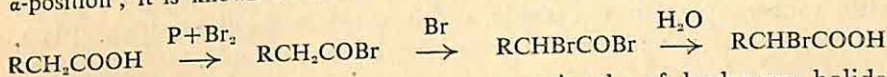


Direct halogenation replaces the hydrogen of the α -carbon atom. Thus, propionic acid, on chlorination, yields $CH_3CHClCOOH$, but not CH_2ClCH_2COOH . In the hydrocarbon chain, chlorine, as a rule, first attacks the carbon poorest in hydrogen. Substitution by iodine is not

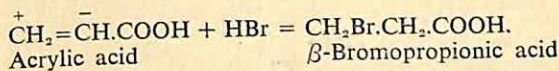
possible (*cf.* paraffins, p. 71). Iodofatty acids are commonly prepared by heating the corresponding chloro-derivatives with potassium iodide:



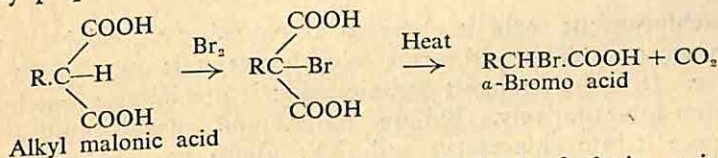
Chlorination or bromination of higher fatty acids is not, however, easy. Acid chlorides are more conveniently brominated; the products are then hydrolysed to obtain the α -bromo acids. Or, liquid bromine is allowed to drop on the acid and red phosphorus. The mixture is warmed and then treated with water to get the α -bromo acid. Substitution invariably takes place in the α -position; it is known as **Hell-Volhard-Zelinsky (H.V.Z.) reaction**.



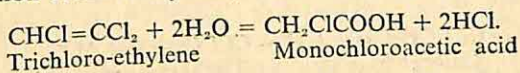
(2) α,β -unsaturated acids take up a molecule of hydrogen halide to form β -halogen acids (*cf.*, reaction of ethylene with halogen acids, p. 58). This is against Markownikoff's Rule (p. 62). Iodo-fatty acids are thus made easily.



(3) From alkyl malonic acids, the halogen-substituted acids may be easily prepared by halogenation and heating:

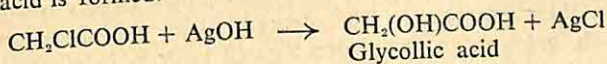


(4) Monochloroacetic acid is also made by hydrolysing trichloro-ethylene (obtained from acetylene) with 75% H_2SO_4 at 140° .

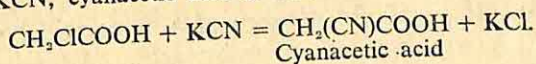


Monochloroacetic acid forms colourless needles (m.p. 62°), soluble in water; it corrodes the skin. It is much stronger than acetic acid (p. 102); it reacts with alkalis, zinc, alcohols (in the formation of esters), etc. Chloroacetic acid is a valuable sterilising agent; it is used in making synthetic indigo and carboxymethylcellulose and also in organic synthesis. The halogen atom can be replaced by $-\text{OH}$, $-\text{CN}$, $-\text{NH}_2$ groups etc., as in alkyl halides (pp. 73-75):

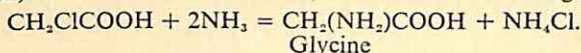
(i) On heating with aqueous KOH or moist silver oxide, hydroxyacetic acid or glycollic acid is formed:



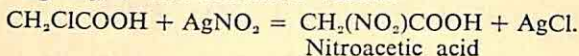
(ii) With KCN, cyanacetic acid is obtained:



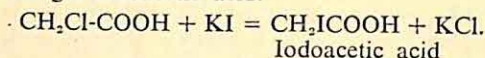
(iii) With alcoholic ammonia, aminoacetic acid or glycine is produced :



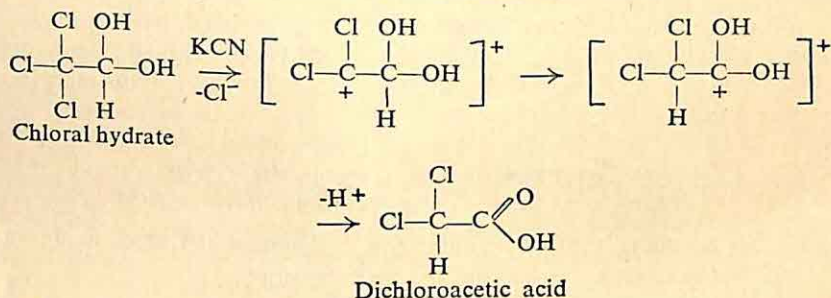
(iv) With AgNO_3 , a nitro-derivative results:



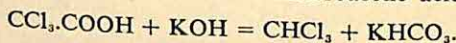
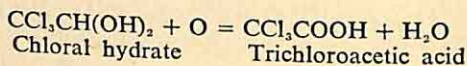
(v) With KI , we get iodoacetic acid:



Dichloroacetic acid is best prepared by boiling chloral hydrate with aqueous potassium cyanide. It is a colourless liquid (b.p. 194°), soluble in water, and resembles monochloroacetic acid.



Trichloroacetic acid is prepared by oxidising chloral hydrate with conc. nitric acid. The acid forms colourless crystals (m.p. 57.5°), highly corrosive. It is the strongest organic acid; it precipitates proteins from a solution quantitatively. Boiling water, and more rapidly, alkalis decompose it into chloroform and CO_2 . Acids having strong electro-negative groups in the α -position behave likewise (cf. malonic acid, Chapter XXIII).



The physical constants of these acids (and acetic acid) are given below :

Name	sp. gr.	m.p. $^\circ\text{C}$	b.p. $^\circ\text{C}$	$\text{K} \times 10^3$
Acetic acid	1.055	16.7	118	.0186
Monochloroacetic acid	1.37	62	189	1.55
Dichloroacetic acid	1.536	11	194	51.4
Trichloroacetic acid	1.617	57.5	197.5	1210.0

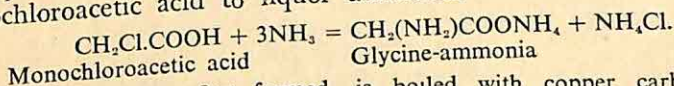
Bromo- and iodoacetic acids are all known; they closely resemble chloroacetic acids in their properties. The strength of an acid increases, on introduction of each halogen, in the order $\text{F} > \text{Cl} > \text{Br} > \text{I}$ (cf. p. 102). Ethyl monoiodoacetate, $\text{I.CH}_2\text{COOC}_2\text{H}_5$, was used in the war of 1914-18 as a tear-gas.

Amino-acids.—If an alkyl hydrogen of a fatty acid be replaced by an amino ($-\text{NH}_2$) group, we get an amino-acid. Aminoacetic acid is

$\text{CH}_2(\text{NH}_2)\text{COOH}$. Any compound containing one or more amino groups and one or more carboxyl groups is an amino-acid. α -Amino-acids are the building stones of animal and vegetable proteins, so essential for our existence. They are consequently obtained when proteins are hydrolysed. So far about 25 such amino-acids have thus been isolated. Most of them are crystalline; the simpler members are soluble in water. Amino-acids are generally sparingly soluble in alcohol and ether. Except glycine, they are all optically active (*vide infra*). Amino-acids with one acidic and one basic group, react almost neutral in aqueous solution. They form salts both with acids and bases. Hence they are amphoteric and used as buffers. The $-\text{NH}_2$ group is far more strongly bound in amino-acids than in acid amides. Thus acetamide is hydrolysed by boiling alkali (p. 166), but not amino-acetic acid. No ammonia is evolved when amino-acids are boiled with caustic alkalis. Some are sweet, many tasteless and others bitter. Their copper salts are blue, generally crystalline and insoluble in water; so they are useful for the isolation and purification of amino-acids. Many form well-defined molecular compounds with metallic salts—their different solubilities are utilised for the separation of amino-acids.

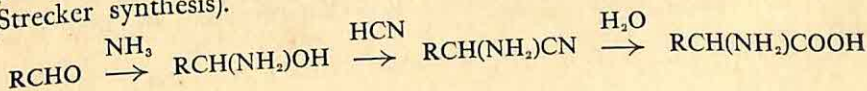
The simplest amino-acid, *viz.* amino-formic or carbamic acid, NH_2COOH , is unknown in the free state; its ammonium salt, $\text{NH}_2\text{COONH}_4$, is obtained by the direct union of CO_2 and NH_3 . Alkyl carbamates or urethanes are also known. The next member, amino-acetic acid, better known as *glycine* or *glycocol*, occurs as hippuric acid (*hippos*, horse) or benzoyl-glycine, $(\text{C}_6\text{H}_5\text{CO})\text{NH}\cdot\text{CH}_2\cdot\text{COOH}$, in the urine of herbivorous animals, and as betaine or trimethylglycine in the beet-root molasses. Methyl-glycine or sarcosine is a decomposition product of caffeine, present in tea leaves. Glycine finds use in photography, pharmacy and varnish making.

Glycine, $\text{CH}_2(\text{NH}_2)\text{COOH}$, represents 33·3% of silk and 10% of wool; it may be obtained by boiling glue or gelatine with dilute H_2SO_4 or NaOH . But it is commonly prepared by slowly adding monochloroacetic acid to liquor ammonia.

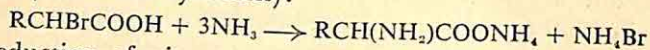


Glycine-ammonia, first formed, is boiled with copper carbonate. On cooling, copper glycine separates, which is dissolved in boiling water and glycine liberated by passing H_2S . Copper sulphide is filtered off, and glycine crystallised from the filtrate. Some di- and tri-glycollamic acids, $\text{NH}(\text{CH}_2\text{COOH})_2$ and $\text{N}(\text{CH}_2\text{COOH})_3$, are also formed. This is a general method for obtaining amino-acids. α -Chloropropionic acid thus yields alanine, $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$, with ammonia.

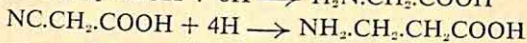
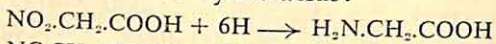
An aldehyde or a ketone reacts with NH_3 and then with HCN to give an amino-nitrile which, by acid hydrolysis, gives an α -amino-acid (Strecker synthesis).



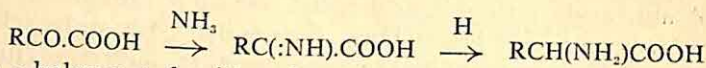
α -Halogeno-acids and excess of NH_3 form ammonium salt of an amino-acid (Hofmann synthesis):



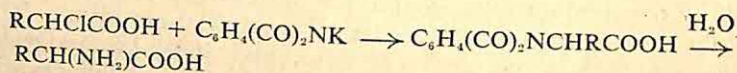
By reduction of nitro- or cyano-acids:



By reducing an α -keto-acid in presence of NH_3 with sodium and alcohol:

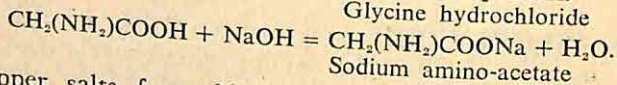
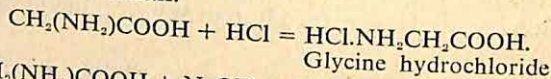


An α -halogenated acid and pot. phthalimide react at 150° to form a substituted phthalimide which, on acid hydrolysis, yields an amino-acid (Gabriel synthesis):

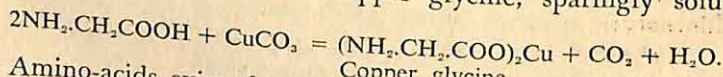


Properties.—Glycine is a colourless, crystalline solid (m.p. 236° with decomposition), readily soluble in water. It gives a deep red coloration with ferric chloride, and has a sweet taste whence the name glycocholl (*glukus*, sweet; *kolla*, glue). The apparent dissociation constants at 25° for glycine are $K_a = 1.8 \times 10^{-10}$ (for the acid) and $K_b = 2.6 \times 10^{-12}$ (for the base); so it reacts slightly acid. The pH at which these ionisations are equal is called the *iso-electric point*. The iso-electric points of aspartic acid, glycine, histidine and arginine are 2.77, 5.97, 7.59 and 10.76 respectively. In our body, glycine helps the elimination of toxic substances by conjugation.

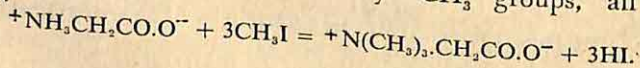
Reactions.—(1) It is amphoteric, forming a hydrochloride with HCl, and a salt with alkali.



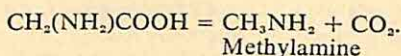
(2) Copper salts form blue copper glycine, sparingly soluble in water.



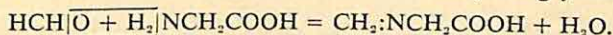
(3) Amino-acids exist almost exclusively as the salt-like double ion $^+\text{NH}_3\text{R}\cdot\text{COO}^-$, called zwitter-ion (or dipolar ion). They are not, therefore, true amino-acids but rather internal ammonium salts. Glycine is more correctly represented by $^+\text{NH}_3\cdot\text{CH}_2\cdot\text{COO}^-$. The Raman spectrum of glycine shows the presence of a dipolar ion in it. This is supported by the fact that amino-acids have high melting points and are generally insoluble in organic solvents, but readily soluble in water. They are usually more soluble in salt solutions than in pure water, and exhibit many other characteristic properties of salts. Furthermore, CH_3I replaces three H-atoms in glycine by $-\text{CH}_3$ groups, all linked to nitrogen:



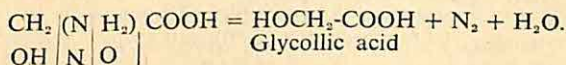
(4) Heated with soda-lime, it decomposes into methylamine and CO_2 .



(5) With formaldehyde, glycine forms methyleneglycine:



(6) Nitrous acid converts it into a hydroxy-acid like a primary amine (q.v.); liberation of nitrogen is quantitative:



Van Slyke's method for the estimation of free amino groups in proteins is based on this reaction. Obviously, half the total volume corresponds to the amount of nitrogen from the amino groups.

Glycine like other amino-acids cannot be directly titrated with acids or alkalis. With *neutral* formaldehyde, it is first converted into methyleneglycine, $\text{CH}_2\text{:N-CH}_2\text{-COOH}$, which is then titrated with alkali using phenolphthalein as indicator.

Aminopropionic acid occurs in two isomeric forms, viz.,

$\text{CH}_2(\text{NH}_2)\text{CH}_2\text{COOH}$ (β -acid) and $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$ (α -acid). The latter, called **alanine**, represents 21% of silk. It is dextro-rotatory, decomposes at about 297° and gives lactic acid with HNO_2 . Alanine as also other amino-acids behaves like glycine.

Serine, β -hydroxy- α -amino-propionic acid, $\text{HOCH}_2\text{CH}(\text{NH}_2)\text{COOH}$, is obtained in the racemic form (it is laevo-rotatory but racemises readily) when proteins such as casein, gelatine, silk-fibroin, etc., are hydrolysed with acids. About 10% of silk is serine (Latin, *sericus*, silk). The racemic form decomposes at 246° and tastes sweet.

Valine, α -amino-isovaleric acid, $(\text{CH}_3)_2\text{CHCH}(\text{NH}_2)\text{COOH}$, is a constituent of casein, zein, penicillins, etc., and consequently obtained when they are hydrolysed. It forms about 3% of silk and 4% of wool. It melts at 315° with decomposition.

Leucine α -amino-isocaproic acid, $(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{NH}_2)\text{COOH}$, occurs in many animal products (e.g., in the pancreas) and is an ingredient of casein, haemoglobin, wool (8.7%), etc. It forms glistening plates (m.p. 270°), sparingly soluble in water. **Isoleucine**, $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{NH}_2)\text{COOH}$, is a structural isomer but not an 'iso' compound.

Arginine, $\text{NH}_2\text{C}(\text{NH})\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$, occurs abundantly (87%) in salmine (in salmon sperm) and forms about 6% of wool and 1% of silk. Many vegetable proteins contain arginine.

Aspartic acid, amino-succinic acid, $\text{HOOCCH}_2\text{CH}(\text{NH}_2)\text{COOH}$, gives with HNO_2 , malic acid. Due to the presence of one $-\text{NH}_2$ and two $-\text{COOH}$ groups, it is acidic. It occurs in *Asparagus officinalis* and other plants, and also in wool and silk.

Glutamic acid. α -amino-glutaric acid, $\text{HOOCCH}(\text{NH}_2)\text{CH}_2\text{CH}_2\text{COOH}$, is present in many vegetable and animal proteins, and forms 10.5% of wool and 1.8% of silk. It represents more than 40% of the protein of wheat. It is crystalline and decomposes at about 202° . Mono-sodium glutamate is used as condiment and also for flavouring foods.

Tyrosine, $\text{HOC}_6\text{H}_4\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$, occurs in cheese (Greek *tyros* cheese), spleen, silk (9.6%) and pancreas. It melts at 235° and is sparingly soluble in water.

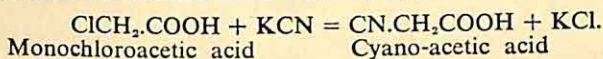
Phenylalanine, $C_6H_5CH_2CH(NH_2)COOH$, is found in gelatin, egg albumin, cheese, etc. Wool has 2.3% of it and silk 1.3%.

Tryptophan, $C_8H_6N.CH_2.CH(NH_2)COOH$, occurs in most proteins but not in gelatin and zein and is made by digesting casein with trypsin. It melts at 289° with decomposition. It is α -indole- β -aminopropionic acid, and gives indole and skatole on decomposition. Acid hydrolysis of proteins destroys tryptophan.

Eight amino-acids are regarded as essential for protein synthesis in our body as normal growth is hampered in their absence. These have to be supplied through protein diet as our system cannot apparently synthesise them. The minimum daily requirement in grams of these acids in l-form for men are: leucine (1.10), methionine (1.10), phenylalanine (1.10), lysine (0.80), valine (0.80), isoleucine (0.70), threonine (0.50) and tryptophan (0.25).

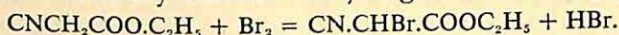
Cyano-acids.—If a cyano group (-CN) replaces an alkyl hydrogen of fatty acids, we get cyano-acids. Of these, cyano-acetic acid is important; the -CN group largely increases the reactivity of the molecule. This is utilised in various organic syntheses.

Cyano-acetic acid, $CH_2(CN).COOH$, is conveniently prepared by treating monochloroacetic acid with KCN.

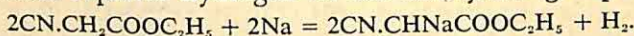


It is also obtained as the potassium salt during the preparation of ethyl malonate (q.v.). The acid melts at 66° and is much stronger than acetic acid (K_a at 25° is 3.65×10^{-3}). As an acid, it can be esterified; the cyano-acetic ester, $CN.CH_2.COOC_2H_5$, possessing a -CH₂- group between two negative radicals, is highly reactive. Thus

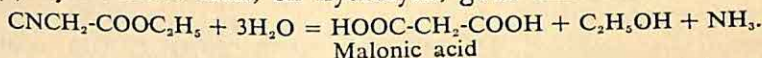
(1) Bromine readily substitutes hydrogen of the CH₂ group:



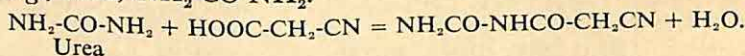
(2) Sodium replaces hydrogen of the methylene group:



(3) Cyano-acetic ester, on hydrolysis, gives malonic acid:



(4) Cyano-acetic acid combines with compounds containing amido groups, e.g., urea, $NH_2-CO-NH_2$.



QUESTIONS

1. How is monochloroacetic acid obtained? What is its commercial use? State with equations the action of aqueous caustic potash, potassium cyanide, and ammonia on monochloroacetic acid.

2. Describe methods for the preparation of halogen-substituted acids of the fatty acids series. State their general properties.

3. How would you estimate the amount of glycine in a sample?

4. Give examples of some synthetic reactions in which cyanacetic ester is employed to give various products.

5. Describe the preparation of any one amino-acid. How would you show that it reacts both as a base as well as an acid? What is the biological importance of amino-acids? B.Sc., Pass, 1950, Allahabad Uni.

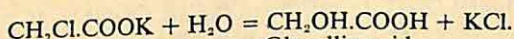
CHAPTER XVII

THE DERIVATIVES OF FATTY ACIDS—IV

The hydroxy-acids.—When one or more hydrogen atoms in the carbon chain of a fatty acid are replaced by hydroxyl groups, hydroxy-acids are formed. Chemically, they are a blend of carboxylic acids and alcohols. Of these, the mono-hydroxy-acids, represented by the general formula, $C_nH_{2n}(OH)COOH$, are the most important. They are usually named by the corresponding fatty acid with the prefix 'hydroxy'; the position of the hydroxyl group is denoted by Greek letters α , β , γ , etc. The first member of the series, hydroxyformic acid, $HO.COOH$, *i.e.*, carbonic acid, behaves as a dibasic acid and is described later with other dibasic acids. The next, hydroxyacetic acid or glycollic acid, $HO.CH_2.COOH$, is the first true representative of the series.

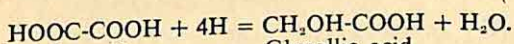
Glycollic acid, $CH_2OH.COOH$, is found in unripe grape, tomato and beet or sugar-cane juice. It is commercially made for cloth-printing, dyeing wool and nylon, de-liming hide and cleaning solutions.

Preparation.—(1) It is conveniently prepared by boiling potassium monochloroacetate with dilute caustic potash or moist silver oxide (p. 181). The solution is evaporated to dryness, and the mass extracted with acetone which dissolves the acid but not KCl .

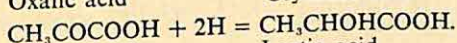


Pot. monochloroacetate Glycollic acid

(2) Technically, glycollic acid is made by the electrolytic reduction of oxalic acid, dissolved in dilute sulphuric acid, using lead electrodes. Aldehydic or ketonic acids give hydroxy-acids on reduction.

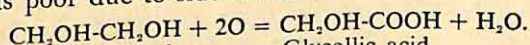


Oxalic acid Glycollic acid



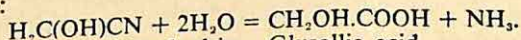
Pyruvic acid Lactic acid

(3) A dihydric alcohol, on mild oxidation, gives a monohydroxy-acid; dilute HNO_3 oxidises ethylene glycol to glycollic acid (p. 110). The yield is poor due to side-reaction.



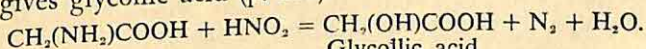
Ethylene glycol Glycollic acid

(4) Cyanhydrins from aldehydes or ketones, on hydrolysis, form hydroxy-acids:



Formaldehyde cyanhydrin Glycollic acid

(5) Amino-fatty acids react with HNO_2 and yield hydroxy-acids; glycine gives glycollic acid (p. 185).



Glycine Glycollic acid

(6) On heating at $160^\circ-170^\circ$ under pressure (above 300 atmos.) in presence of a catalyst such as H_2SO_4 , formaldehyde, carbon monoxide and water form glycollic acid. It is an industrial process. Replac-

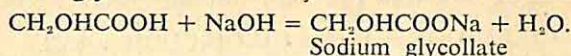
ing water by methanol, we get methyl glycolate which is reduced to glycol commercially.



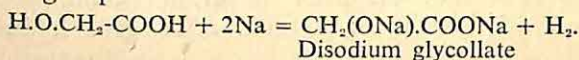
These methods, except (6), are applicable for the preparation of other hydroxy-acids. By (4), however, only α -hydroxy-acids can be obtained.

Properties.—Hydroxy-acids are mostly liquids at ordinary temperature; glycollic acid is a crystalline solid (m.p. 80°) soluble in water, ethanol and ether. They are more soluble in water than the corresponding fatty acids owing to the presence of an additional -OH group, and less volatile. Hydroxy-acids are stronger than the corresponding fatty acids. Glycollic acid has a dissociation constant 1.49×10^{-4} at 25° , and acetic acid 1.86×10^{-5} . The electrophilic -OH group attracts the electrons away from the hydrogen of the carboxyl group and allows it to escape as proton more readily (*cf.* chloro-acetic acids, p. 102). The nearer the -OH group to the -COOH, the greater the strength. As acids, they form salts, acid amides, esters, etc., while the alcoholic -OH group can be replaced by an alkyl or acyl radical and so on. Their general chemical behaviour is represented by glycollic acid.

Reactions of glycollic acid.—Glycollic acid forms salts with alkalis:



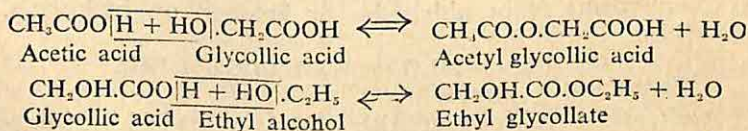
(2) Metallic sodium replaces the hydrogen of both alcoholic and carboxylic -OH groups:



(3) Similarly, PCl_5 replaces both carboxylic and alcoholic -OH groups giving chloroacetyl chloride which readily gives chloroacetic acid with water.



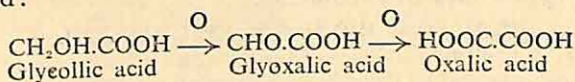
(4) Glycollic acid reacts with an acid as an alcohol, and with an alcohol as an acid. In both cases, an ester is formed; in the former, a free -COOH group, and in the latter, a free alcoholic group, remain intact.



(5) Hydrogen chloride converts glycollic acid into chloroacetic acid; but HI reduces it to acetic acid on heating:



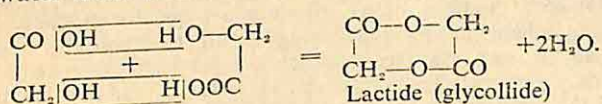
(6) On oxidation, glycollic acid first gives an aldehydic and then, a dibasic acid:



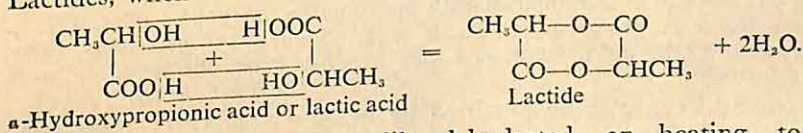
But if it is a secondary alcoholic group, as in α -hydroxypropionic acid, first a ketonic acid and then a fatty acid is obtained.



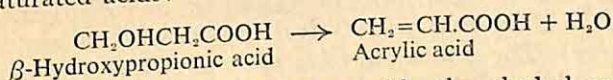
(7) Hydroxy-acids readily lose water on heating; the manner depends upon the position of the -OH group. Glycollic acid, at 100° , forms a cyclic ester anhydride (or a *lactide*) by the elimination of 2 mols. of water from 2 mols. of the acid:



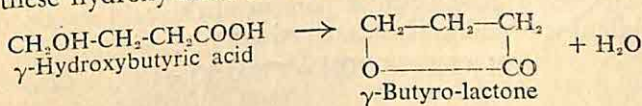
Here the alcoholic -OH group of one esterifies the -COOH group of the other. Glycollic acid also forms other anhydrides, e.g., $\text{HOCH}_2\text{---COOCH}_2\text{COOH}$. All α -hydroxy-acids behave likewise e.g., lactic acid gives the lactide when heated to 140° under reduced pressure. Lactides, when boiled with water, give back α -hydroxy-acids.



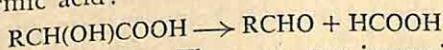
β -Hydroxy-acids are readily dehydrated, on heating, to yield α,β -unsaturated acids:



In the case of γ - and δ -hydroxy-acids, the alcohol and acid groups of the same molecule readily form an inner ester, called *lactone*. In fact, most of these hydroxy-acids occur as lactones.



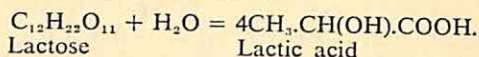
(8) Heated with dilute H_2SO_4 , α -hydroxy-acids form an aldehyde or a ketone, and formic acid:



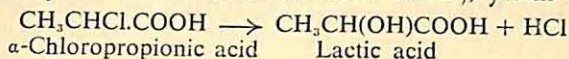
Hydroxypropionic acids.—There are two isomeric acids, α - and β -. The former, called lactic acid (Latin *lac*, milk), is much more important. It was first isolated in 1780 from sour milk by the Swedish apothecary, Scheele.

Lactic acid, $\text{CH}_3\text{CH(OH)COOH}$.—Milk-sugar or lactose is split up into lactic acid by bacteria (*Bacillus lactis acidii*) coming from the

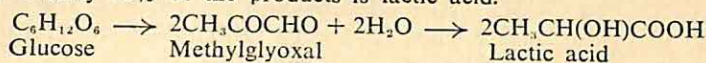
air. That is how lactic acid occurs in sour milk. It is also present in gastric juice, opium and in cucumbers.



Preparation.—Lactic acid may be prepared by methods described under glycollic acid (p. 187). For example, α -chloropropionic acid, on hydrolysis (or by the action of moist silver oxide), yields lactic acid:



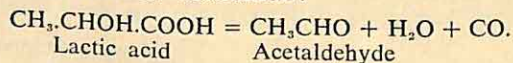
Commercially, however, lactic acid is made from cane-sugar, glucose or starch. Starch must first be hydrolysed to simpler sugars. Germany uses sugars of beet-molasses. To the dilute aqueous solution of the sugar, *B. lactis acidii* is added in the form of sour milk or decaying cheese, and the temperature maintained at 40°-45°. Some nutritive solutions are usually supplied. Powdered chalk is gradually added to the fermenting liquid to neutralise most of the lactic acid formed, as even 1% free acid renders the bacilli inactive. In neutral medium, butyric fermentation sets in. Crystals of calcium lactate, $(\text{C}_3\text{H}_5\text{O}_2)_2\text{Ca} \cdot 5\text{H}_2\text{O}$, separate and are removed. The fermentation is continued for about ten days, by which time all the sugar disappears. No carbon dioxide evolves during this fermentation. Methylglyoxal is believed to be an intermediate product. Nearly 90% of the products is lactic acid.



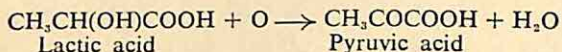
The calcium salt is decomposed with the requisite amount of dilute H_2SO_4 . Calcium sulphate is removed and lactic acid obtained by distillation under reduced pressure. In India, lactic acid may be made from the waste molasses of sugar factories.

Lactic acid can also be obtained by heating glucose or cane-sugar with caustic alkalis.

Properties.—Lactic acid usually exists as a colourless, viscous liquid, the pure acid melting at 18°. It decomposes when heated under ordinary pressure. The acid is miscible with water, alcohol and ether, and forms insoluble calcium and zinc salts. It is much stronger ($K = 13.8 \times 10^{-5}$) than acetic acid. During heating several lactides are formed, e.g., lactic anhydride, $\text{CH}_3\text{CH}(\text{OH})\text{CO} \cdot \text{OCH}(\text{CH}_3)\text{COOH}$, and cyclic lactide (p. 189). And a portion of the acid suffers decomposition to acetaldehyde and carbon monoxide:



Heated to 140° with dilute H_2SO_4 , lactic acid decomposes into acetaldehyde and formic acid; conc. H_2SO_4 effects the same change but more readily, the formic acid being further decomposed into CO and H_2O . Lactic acid yields iodoform with iodine and alkali, as all compounds containing the $\text{CH}_3\text{CO}-\text{C}$ or $\text{CH}_3\text{CHOH}-$ group do (p. 80). Like glycollic acid, it behaves both as an acid and as an alcohol, and reacts likewise with alcohol, phosphorus pentachloride, halogen acids, etc. On oxidation with dilute H_2O_2 and FeSO_4 , lactic acid gives pyruvic acid, a ketonic acid, which shows the presence of a secondary alcoholic group. But with KMnO_4 it forms acetic acid.



Uses.—Lactic acid is an acidulant in food or beverage. Antimony lactate is used in dyeing wool and in calico printing. It removes lime from hides; the tanning industry consumes most of the lactic acid. Ethyl lactate is employed in making lacquer varnish, being a high-boiling solvent for both cellulose acetate and nitrate. Calcium lactate is used in medicine for calcium deficiency, as a blood coagulant and also in baking powder. Ferrous lactate is an iron tonic, and silver lactate which is less caustic than silver nitrate, is an antiseptic and astringent.

Polarised light and optical activity.—Lactic acid is theoretically important, being one of the simplest compounds which exhibit *optical activity*. It would appear from the formula that there should be only one lactic acid, but in fact there are three. These isomers are exactly similar in their chemical reactions and most physical properties, but differ in their behaviour towards polarised light. Such a phenomenon where compounds, having apparently the same structure, differ in their optical properties, is known as *optical isomerism*, a form of *stereo-isomerism* (Greek *stereos*, solid). The compounds are called optical isomers (*vide* p. 249-50).

According to the wave theory, an ordinary ray of light is considered to vibrate in all directions at right angles to its path. If a beam of mono-chromatic light (*e.g.*, the yellow light from sodium vapour lamp) be passed through crystals of Iceland spar (calcite) or tourmaline, it splits up into two, each vibrating in *one plane only*. The light is said to be polarised, and the two newly formed rays have different refractive indices. Consequently, by combining two prisms of Iceland spar, suitably cut, it is possible to have total internal reflection for one of the rays and allow the other to pass on. Such a combination of prisms is called a *Nicol prism* (after William Nicol, a physicist of Edinburgh). If another Nicol prism be placed in the path of the transmitted polarised ray, the effect is interesting. If the axis of the second prism be parallel to that of the first, the polarised beam passes through it with full intensity, but if the prism be rotated through 90°, the polarised ray is completely cut off due to total reflection. The second prism, called *analyser*, thus enables us to find the plane of vibration of the polarised ray. In intermediate positions of the analyser, light of varying intensity will, of course, pass through.

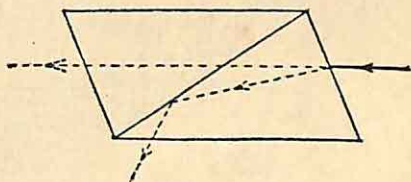


Fig. 33. Nicol prism.

To begin with, the polariser (the first Nicol prism) and the analyser are placed in the same axial line; the polarised ray passes through the analyser with undiminished intensity. Now, if between these two, a solution, say of turpentine or of glucose be placed, it is

found that the analyser has to be rotated through a certain angle in order to get the original light. These solutions must have rotated the polarised ray either to the left, or to the right. This property, by virtue of which many organic as also some inorganic compounds turn the plane of polarised light either in clockwise or anticlockwise direction, is known as *optical activity*. Compounds which turn the plane towards the right, are called *dextro-rotatory*, while those which do so towards the left, are *laevo-rotatory*. The construction of the polarimeter or polariscope which measures such rotation, is based on these facts.

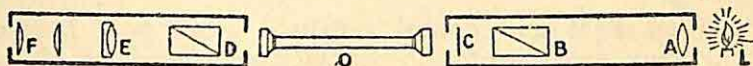


Fig. 34. Optical parts of the polarimeter.

In the rough sketch of the polarimeter (Fig. 34), L is the source of monochromatic light which emerges out parallel after passing through the lens, A and is incident upon the polariser, B. O, an observation glass tube with glass ends, contains the substance in solution; D is the analyser. The field of view is observed through the telescope EF, connected to a graduated circular scale. The analyser and the circular scale rotate *simultaneously*. The zero reading of the circular scale is first determined with water, noting

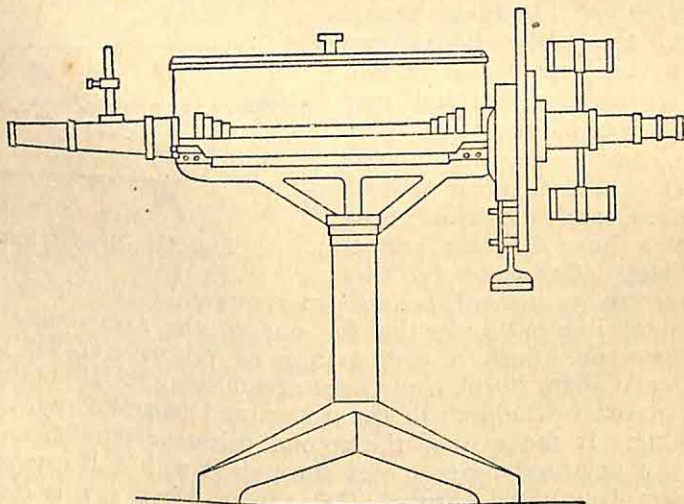


Fig. 35.—Laurent's polarimeter.

the minimum illumination point. The tube is now filled with the solution to be examined, and the scale rotated until the minimum illumination point is again reached. The amount and direction of rotation are known from the scale.

The magnitude of rotation depends on (i) nature of the compound, (ii) concentration of the solution, (iii) length of the

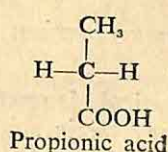
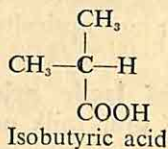
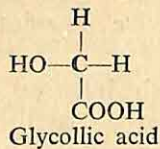
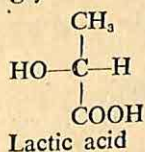
solution column traversed by the polarised light, (*iv*) wave-length of light used, (*v*) temperature of solution and (*vi*) medium or solvent. For comparison of the rotatory powers, therefore, a standard has to be maintained. At a definite temperature and for a particular wave-length of light, the rotation produced by a substance in solution is proportional to the length of the liquid column. The *specific rotation* or rotatory power of a substance is defined as the angle of rotation produced by 1 decimeter length of the solution having 1 g. of the substance per c.c. If A denotes the rotation produced by a substance for a light of wave-length, λ , at a temperature, t , by a layer of solution, 1 dm. long, and having c g. per 100 c.c. of the solution, then its specific rotation,

$$\left[\alpha \right]_{\lambda}^t = \frac{A \times 100}{1 \times c}$$

The *molecular rotation* is obtained by multiplying the specific rotation by the molecular weight of the substance.

It is interesting to note that the optically active substances first discovered were all inorganic—some rock crystals, quartz, etc. Later on, crystals of potassium bromate, potassium chlorate and sodium periodate were found to be optically active. Optical activity in such cases is due to the *crystalline structure*, because as soon as the crystalline structure is destroyed by melting or dissolving in a liquid, the optical activity disappears. Some organic compounds as well, e.g., benzil, $C_6H_5CO.CO.C_6H_5$, exhibit optical activity only in crystalline state.

J. B. Biot in 1815 first observed (Louis Malus, a French military engineer, discovered polarisation of light in 1808) that organic compounds such as oil of turpentine, sugar, camphor, tartaric acid, etc. can rotate the plane of polarised light in liquid or dissolved state. Optical activity of most organic compounds (and also of some inorganic compounds) depends on molecular structure. Practically all optically active organic compounds contain one or more carbon atoms whose four valencies have been satisfied by four *different* monovalent groups or atoms. Such a carbon is called *asymmetric*. These compounds show optical activity in solution, and also in liquid or gaseous form. If any two of such groups or atoms are made the same, the substance becomes optically inactive. Thus lactic acid is optically active but glycollic, isobutyric and propionic acids are not.



In the year 1874, van't Hoff (1852-1911) and Le Bel (1847-1930) (one a Dutch and the other a French but both pupils of Wurtz in Paris) independently, and almost simultaneously, advanced a theory correlating structure with optical activity and explained the

optical isomerism of carbon compounds. According to them, the isomerism is due to different spatial arrangement of atoms or radicals in the molecule. They assume that the carbon atom lies at the centre of a regular tetrahedron, and the four valencies are directed towards its summits. This view of tetrahedron structure has been supported by X-ray studies. Four *different* groups or atoms, attached to a carbon, give rise to optical activity. We may, therefore, predict optical activity from molecular structure. It may be noted, however, that the carbon atom itself is not asymmetric but the molecule, containing such an atom, is asymmetrically arranged. The spatial arrangement of atoms and groups in the lactic acid molecule can be expressed in two ways:

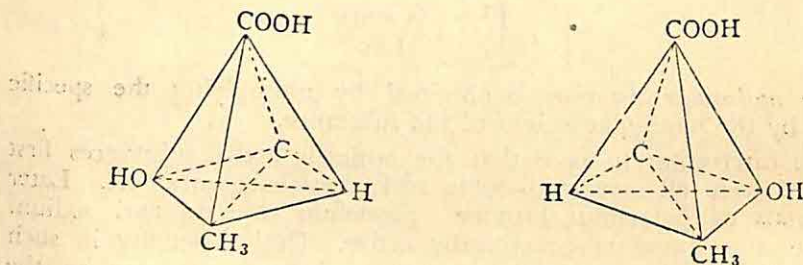


Fig. 36.—Lactic acid molecules.

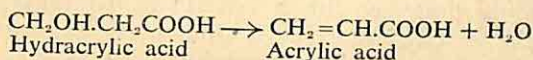
These two models are not superimposable, *i.e.*, it is impossible to turn them so that they may appear identical. None can be divided by a plane into two identical halves. They are like the right and the left hand, or an object and its mirror image. Technically, they are called *enantiomorphs*. It is not possible to say which is dextro-rotatory or which is lævo-; a choice is arbitrarily made for convenience. The *dextro* and *lævo* forms are denoted by the prefixes d- and l-, or by +ve and -ve sign respectively. Their sp. rotations are equal in magnitude but opposite in direction. An equimolecular combination of dextro- and lævo-form gives the inactive variety. Lactic acid, a classical example, occurs in three forms, d-, l- and inactive or dl-. If there be more than one asymmetric carbon atom in the molecule, we have a larger number of stereoisomers. Tartaric acid (Chapter XXV) is an example. Hundreds of optically active compounds are now known—only in rare cases, however, an exception to van't Hoff and Le Bel's theory has been found. Compounds like inositol contain no asymmetric carbon but are optically active in solution (*vide* Chapter XXX).

Optical isomers of lactic acid.—(i) Inactive or dl-lactic acid: Ordinary lactic acid of sour milk or that prepared by fermentation or by synthetic methods, is optically inactive. It can, however, be resolved by suitable methods into the active forms—dextro and lævo. (ii) l-Lactic acid is obtained from the dl-acid by resolution (*vide* chapter XXV). (iii) d-Lactic acid (also called sarcocollactic acid) results from the breakdown of glycogen in muscles. The transformation is reversible;

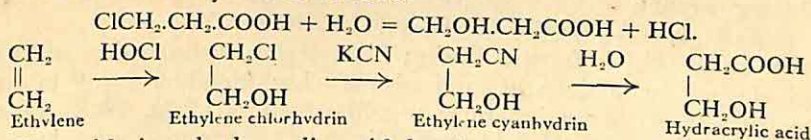
during rest, most of the sarcolactic acid is converted back into glycogen. The three isomers have similar chemical properties.

Sarcolactic acid, para- or d-lactic acid, $\text{CH}_3\text{CHOHCOOH}$, occurs in muscles (*sarkos*, flesh) and was isolated therefrom by Berzelius in 1808. It occurs in meat extract; from the extract albumin is precipitated with alcohol. The alcohol is distilled off and sarcolactic acid taken up with ether from the acidified residue. With muscular activity, the content of sarcolactic acid in tissues rapidly increases, fatigue is apparently due to its accumulation. Sarcolactic acid is a crystalline solid (m.p. 26°), chemically similar to ordinary lactic acid. It differs from the latter in (i) having a higher m.p. (ii) being dextro-rotatory, $[\alpha]_D = +3.8^\circ$. (iii) forming a zinc salt with 2 mols. of water of crystallisation (instead of 3 mols.), which is more soluble in water, and (iv) giving a calcium salt with 4 mols. of water (instead of 5 mols.), which is less soluble in water.

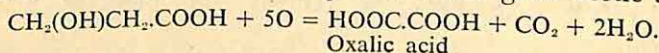
Hydracrylic acid, β -hydroxypropionic acid or ethylene lactic acid, $\text{CH}_2(\text{OH})\text{CH}_2\text{COOH}$, a structural isomer of lactic acid, is a thick syrupy liquid, soluble in water. It is optically inactive (having no asymmetric carbon) and exists only in one form. On heating alone or with dilute H_2SO_4 , it loses a molecule of water (like all β -hydroxy acids, p. 189) forming acrylic acid whence the name (*cf.*, lactic acid which forms a lactide).



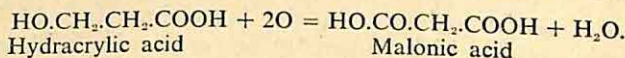
It may be prepared by hydrolysing β -chloropropionic acid, and synthesised from ethylene as follows:



On oxidation, hydracrylic acid breaks up into oxalic acid, carbon dioxide and water (*cf.*, lactic acid, p. 189, which gives acetic acid).

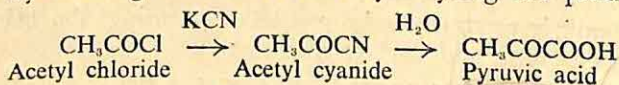


On warming with chromic acid, however, it forms malonic acid:

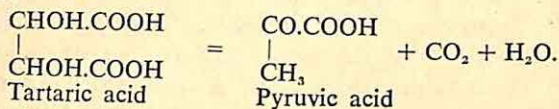


The monobasic ketonic acids contain both the ketonic and the carboxyl group in the molecule. Pyruvic acid or α -ketopropionic acid is the simplest member of the series.

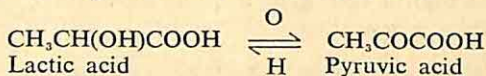
✕ **Pyruvic acid**, $\text{CH}_3\text{CO}.\text{COOH}$, may be prepared from acetyl chloride by treating with KCN and hydrolysing the product (p. 163):



Its constitution follows from this synthesis. Any α -ketonic acid can thus be obtained. More readily, however, pyruvic acid is made by distilling tartaric acid alone or better, with KHSO_4 . Here tartaric acid behaves as a β -hydroxy acid. Berzelius thus obtained the acid for the first time. Hence the old names, pyroracemic or pyrotartaric acid for pyruvic acid.



Oxidation of lactic acid with dilute H_2O_2 and a little FeSO_4 yields pyruvic acid (p. 190). Here the secondary alcoholic group is oxidised to a ketonic group (p. 124). Pyruvic acid may be reduced back to lactic acid with sodium amalgam and water, or zinc and acetic acid.

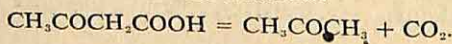


Pyruvic acid is a colourless liquid (b.p. 165°) with a pungent smell, miscible with water or alcohol in all proportions. As a ketone, it gives a bisulphite compound, a phenylhydrazone and an oxime; while as an acid, it forms salts, esters, etc. On oxidation with dilute permanganate, it splits into carbon dioxide and acetic acid: $\text{CH}_3\text{COCOOH} + \text{O} = \text{CH}_3\text{COOH} + \text{CO}_2$. Pyruvic acid and in fact, all α -ketonic acids (but not other ketonic acids) reduce ammoniacal silver nitrate like aldehydes. This is due to the ease with which the acid loses CO_2 on heating alone, warming with H_2SO_4 or heating its salts with carbonates; the acetaldehyde formed then acts as the reducing agent:



Pyruvic acid is formed during biological transformation of sugars into alcohol or lactic acid, and also during metabolism of fats and proteins. It gives the iodoform test like lactic acid (p. 190). Due to the presence of the electrophilic $-\text{CO}-$ group, pyruvic acid ($k = 5.6 \times 10^{-3}$) is much stronger than propionic acid, $\text{CH}_3\text{CH}_2\text{COOH}$ ($k = 0.014 \times 10^{-3}$). Atophane, a remedy for gout, is made from pyruvic acid.

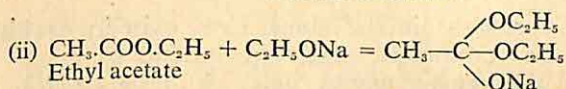
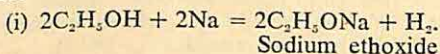
Acetoacetic acid, $\text{CH}_3\text{CO.CH}_2\text{COOH}$, the simplest β -ketonic acid, occurs in traces in normal human urine and abundantly in the urine of diabetic patients. In the body, butyric acid is oxidised to acetoacetic acid which normally gives acetic acid on further oxidation; in diabetics, however, due to defective oxidation, it is decarboxylated to acetone. Acetoacetic acid and acetone thus occur in their blood and urine; their toxic effect may cause death. The acid is unstable and obtained only by careful hydrolysis of its ester. It is a syrupy, hygroscopic liquid, miscible with water and gives a deep red-violet coloration with dilute FeCl_3 (difference from acetone). With iodine and alkali, it produces iodoform. On warming, the acid rapidly breaks up into acetone and carbon dioxide:



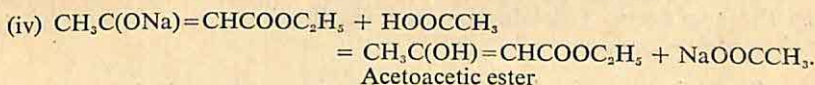
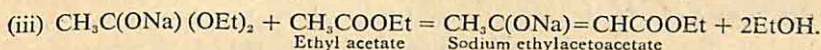
Acetoacetic ester, ethyl acetoacetate, $\text{CH}_3\text{CO}.\text{CH}_2\text{CO}.\text{O}.\text{C}_2\text{H}_5$, unlike the acid, is quite stable. It is an important synthetic reagent, and prepared from ethyl acetate by the action of sodium in presence of a little ethyl alcohol. In his attempt to replace a second hydrogen of acetic acid by sodium, Geuther in 1863 treated ethyl acetate with sodium and obtained a compound, which, on acidification, gave what we now call acetoacetic ester.

Preparation.—Clean sodium in thin slices is added to ten times its weight of pure and dry ethyl acetate containing a little ethyl alcohol, taken in a flask fitted with a reflux condenser. The reaction, slow at the outset, becomes gradually vigorous. The liquid boils and hydrogen evolves. The sodium derivative of acetoacetic ester forms a brown mass with sodium ethoxide. This is treated with dilute acetic acid (1:1), to decompose the sodium derivative. The mass is then poured into a saturated sodium chloride solution, when ethyl acetate (unchanged) and ethyl acetoacetate separate as an oily layer. This is removed and distilled, ethyl acetate (b.p. 78°) goes off first. The fraction between 175°-185° is almost pure acetoacetic ester which may be further purified by re-distillation under reduced pressure.

The reaction is rather complex. L. Claisen (1851-1930) showed that sodium and alcohol may be replaced by sodium ethoxide. According to him, the stages are



Intermediate additive compd.



Two ethyl acetate molecules are thus coupled, with elimination of a molecule of alcohol, to form ethyl acetoacetate. Reactions resulting in a longer carbon chain, with or without elimination of water, alcohol, etc., are called *condensation reactions* (p. 139). A condensation between two molecules of the same or different esters in presence of sodium ethoxide, as above, is known as **Claisen condensation**.

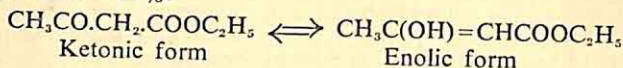
Properties and uses.—Acetoacetic ester is a colourless liquid (*d*, 1.03) boiling at 181° with slight decomposition. It has a pleasant, fruity odour. The ester is only slightly soluble in water but readily dissolves in alcohol and ether. Antipyrine, a febrifuge, is made from acetoacetic ester; pyrazolone dyes are derived from it. It is also used in perfumery.

Acetoacetic ester behaves as a ketone and gives derivatives with HCN, NaHSO_3 , $\text{C}_6\text{H}_5\text{NHNH}_2$, NH_2OH , etc. It also forms β -hydroxybutyric ester, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{COOC}_2\text{H}_5$, on reduction; the keto group is reduced to a secondary alcohol group. On hydrolysis with dilute H_2SO_4 , it yields acetone, alcohol and carbon dioxide. These reactions indicate a keto group, and the ester should be $\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5$.

But metallic sodium liberates hydrogen from the ester as from alcohols. The ester, neutral to litmus, dissolves in alkalis, indicating its acidic nature. It produces a violet-red coloration with FeCl_3 in alcoholic solution like an

enol (*en-* for unsaturation, *ol* for alcohol) having the group, C(OH)=C< , (e.g., phenols). The ester adds on bromine (in alcohol) showing a double bond. With PCl_5 , it gives β -chloro-crotonic ester, $\text{CH}_2\text{CCl=CHCOOC}_2\text{H}_5$. It also forms an unsaturated ether, $\text{CH}_3\text{C(O.CH}_3\text{)=CH.COOC}_2\text{H}_5$, with diazomethane, CH_3N_2 . So it has a hydroxyl group and a double bond. The ester then should be $\text{CH}_3\text{C(OH)=CHCOOC}_2\text{H}_5$.

This anomaly is explained by assuming that the ester is an equilibrium mixture of both ketonic and enolic forms. Molecular refraction and other physical data support this view. It has been shown that 7.5% of the ester at ordinary temperature is in enol form. The degree of enolisation largely depends upon the nature of the solvent, e.g., in glacial acetic acid only 5.7% is enolised but in petrol ether, 46.4%.

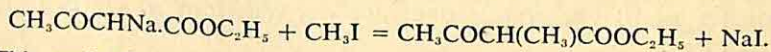


If one be removed (say, the enolic form, by reaction with sodium), the other is partly transformed into the same to attain equilibrium. The keto form has been isolated at -78° by crystallising the keto-enol mixture from light petroleum. It forms long, colourless needles (m.p. -39°) and gives no coloration with alcoholic FeCl_3 , nor does it react with bromine. The enolic form, separated in pure state by distillation under high vacuum, is a colourless oil; it gives coloration with FeCl_3 , and readily takes up bromine. With rise of temperature, the pure forms rapidly pass on to the equilibrium mixture. Traces of alkali derived from ordinary glass vessels catalyse rapidly the inter-conversion of the keto-enol forms. Both are fairly stable in quartz vessels.

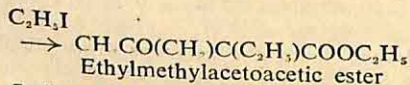
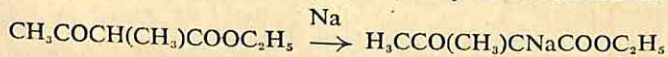
If two isomeric forms, as in the above case, exist in equilibrium, they are said to be tautomeric and the phenomenon is called *tautomerism* (*tauto*, the same; *meros*, part) or *desmotropism*. The less stable one is the labile form. Such changes commonly occur by the 'wandering' of a hydrogen from one polyvalent atom to another within the molecule. Tautomerism, also called *dynamic isomerism* as the two forms exist in dynamic equilibrium, may involve a shift of other atoms or ions.

Synthetic uses of β -ketonic esters.—Sodium replaces hydrogen in β -ketonic esters. This is generally possible when a $-\text{CH}_2-$ group occurs between two negative groups such as $-\text{COOEt}$, $-\text{CN}$, $-\text{CO}$, etc. In acetoacetic ester, two adjacent electrophilic carbonyl groups largely facilitate the escape of the hydrogen in the intermediate methylene group as proton. Acetoacetic ester reacts with sodium forming $\text{CH}_3\text{C(ONa)=CHCOOC}_2\text{H}_5$, a highly reactive solid of great synthetic value. It is best prepared by adding sodium ethoxide (and not metallic sodium) to the ester, no reduction of the ester by nascent hydrogen can take place.

(a) **Synthesis of alkyl acetoacetic esters:** The sodium derivative of ethyl acetoacetate reacts with alkyl iodide, on boiling, to produce a mono-alkyl ethyl acetoacetate:

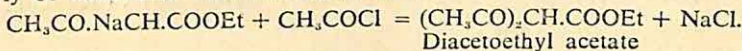


This again forms a sodium derivative—the remaining hydrogen of $-\text{CH}_2-$ group is now replaced. A second alkyl group may be introduced likewise.

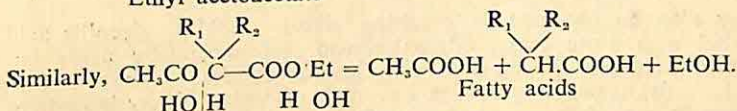
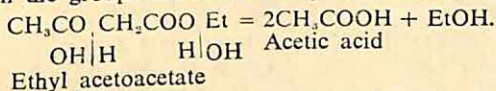


Sodium does not further react with this β -ketonic ester. The alkyl groups

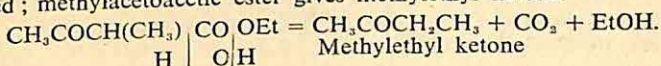
are introduced one after another. Sodium derivatives of β -ketonic esters may similarly be condensed with acid chlorides :



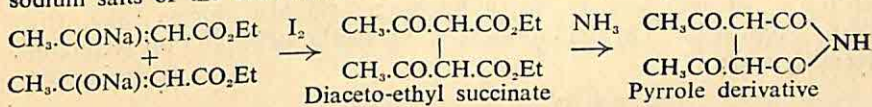
(b) **Synthesis of fatty acids:** (Acid hydrolysis) If the ester or its alkyl derivative be hydrolysed with concentrated alcoholic potash, various fatty acids, depending upon the groups introduced, may be obtained, e.g.,



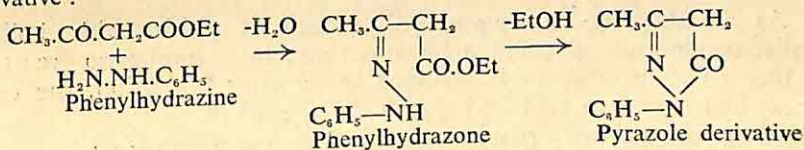
(c) **Synthesis of ketones:** (Ketonic hydrolysis) When the ester or its alkyl derivative is hydrolysed with dilute H_2SO_4 , or dilute aqueous potash, a ketone is formed; methylacetoacetic ester gives methylethyl ketone.



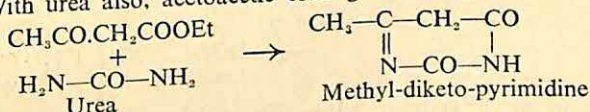
(d) **Synthesis of cyclic compounds:** (i) Pyrrole derivatives result when sodium salts of the ester react with iodine and subsequently with ammonia :



(ii) Phenylhydrazine and ethylacetoacetate finally yield a pyrazole derivative :



(iii) With urea also, acetoacetic ester gives a ring compound :



Lævulinic acid, β -acetylpropionic acid, $\text{CH}_3\text{COCH}_2\text{CH}_2\text{COOH}$, is a γ -ketonic acid, produced by boiling with dilute HCl any sugar containing six (e.g., glucose or fructose) or multiple of six (e.g., cane-sugar or starch) carbon atoms. The acid is obtained pure by vacuum distillation. It is a crystalline solid (m.p. 33°), highly soluble in water. It is used in cotton printing. γ -Ketonic acids are much less reactive than the β - due to the absence of $-\text{CO}-\text{CH}_2-\text{CO}-$ group in them—lævulinic ester does not react with sodium. Lævulinic acid was first obtained from lævulose (or fructose) whence the name.

Aldehydic acids have both $-\text{COOH}$ and $-\text{CHO}$ groups in the molecule; they respond to the typical reactions of these groups. The

3. How can you prepare lactic acid? What reactions show that it is both an alcohol and an acid? Explain the isomerism of lactic acid. Describe its constitution. B.Sc., 1951, Calcutta Uni.; B.Sc., 1947, Nagpur University.

4. What are the general methods for the preparation of hydroxy-acids? Describe their main properties and show how α -, β - and γ -hydroxy-acids behave on heating.

5. Distinguish between tautomerism and stereoisomerism. Explain each fully, and illustrate with at least one example of each. B.Sc. 1947, Benares Hindu Uni.

6. Discuss the mechanism of the formation of aceto-acetic ester. Starting with aceto-acetic ester indicate the steps involved in the preparation of: (a) methyl n-butyl ketone, $\text{CH}_3\text{CO}(\text{CH}_2)_3\text{CH}_3$, (b) n-butyric acid, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$, and (c) n-propyl ethyl acetic acid, $\text{CH}_3\text{CH}_2\text{CH}_2(\text{CH}_2\text{CH}_2)\text{CHCOOH}$. B.Sc., Degree Exam., 1942, Annamalai University.

7. Write a note on tautomerism. B.Sc., 1941, Agra Uni.

8. Describe the characteristic behaviour of α -, β -, γ -hydroxy-, and amino-acids. B.Sc., 1942, Agra Uni.

9. Give a brief historical account of the development of our ideas regarding the phenomenon of optical activity in organic compounds.

10. How is lactic acid obtained in the laboratory? Give an account of the action of heat on α -, β -, and γ -monohydroxy acids. B.Sc. Degree Exam., 1942, Madras Uni.

11. How is ethyl acetoacetate prepared? What is the mechanism of its formation? Outline its principal synthetic applications. B.Sc. Degree Exam., 1942, Travancore Uni.

12. Discuss fully the constitution of acetoacetic ester. How would you use it to synthesise (a) methyl ethyl ketone, (b) propionic acid and (c) valeric acid? B.Sc. Exam., 1946, Benares Hindu Uni.

13. An acid X has 40.0% C and 6.7% H. 0.11 g. of it requires 12.2 c.c. of 0.1 N NaOH for neutralisation; its ethyl ester has a mol. wt. of 118. On heating, X behaves as $2\text{X} = 2\text{H}_2\text{O} + \text{Y}$. Y is a neutral, white solid. What is the structure of Y?

CHAPTER XVIII

THE AMINES

If the hydrogen of ammonia, NH_3 , be replaced by alkyl radicals, we get **amines**. These are, therefore, substituted ammonias. Amines are primary, secondary or tertiary according as 1, 2 or 3 hydrogen atoms respectively are replaced by alkyl groups:

NH_3	RNH_2	R_2NH	$\text{R}_1\text{R}_2\text{R}_3\text{N}$
Ammonia	Primary amine	Secondary amine	Tertiary amine

The characteristic groups in the three classes of amines are $-\text{NH}_2$ (amino), $-\text{NH}-$ (imino), and $>\text{N}-$ (nitrile) respectively. The alkyl radical may be the same or different (giving *mixed amines*), saturated or unsaturated. Amines closely resemble ammonia or caustic alkalis, and represent the commonest of organic bases. Like the parent substance, they readily combine with acids forming additive salts.

NH_3HCl	$\text{CH}_3\text{NH}_2\text{HCl}$	$(\text{CH}_3)_2\text{NH}\text{HCl}$	$(\text{CH}_3)_3\text{NHCl}$
Ammon. chloride	Methylamine hydrochloride	Dimethylamine hydrochloride	Trimethylamine hydrochloride

Besides these, there are the quaternary ammonium compounds, R_4NX , which may be regarded as ammonium salts with the four hydrogen atoms replaced by alkyl groups. Tetramethyl ammonium chloride, $(\text{CH}_3)_4\text{NCl}$, and tetramethyl ammonium hydroxide, $(\text{CH}_3)_4\text{NOH}$, are examples. Like NH_4^+ , NR_4^+ has no free existence, but tetraethyl ammonium, $(\text{C}_2\text{H}_5)_4\text{N}$, has been obtained in liquid ammonia solution. Amines are generally named according to the constituent hydrocarbon radicals; thus $\text{C}_2\text{H}_5\text{NH}_2$ is ethylamine, $\text{CH}_3\text{NH}\text{C}_2\text{H}_5$ is ethylmethylamine and so on. The Geneva System is sometimes used for primary amines e.g., aminoethane, $\text{C}_2\text{H}_5\text{NH}_2$; 1-aminopropane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$, etc.

Isomerism of the amines.—(i) Amines may be isomeric due to isomerism in the alkyl radicals, e.g.,

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ and	$(\text{CH}_3)_2\text{CH}\text{CH}_2\text{NH}_2$
<i>n</i> -Butylamine	Isobutylamine

(ii) The amino group may replace hydrogen at different positions in the same hydrocarbon chain, e.g.,

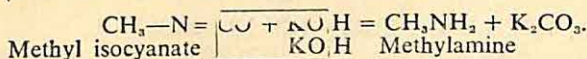
$\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{CH}_3$	and	$\text{CH}_3\text{CH}_2\text{CH}(\text{NH}_2)\text{CH}_3$
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(iii) The same number of carbon and hydrogen atoms (constituting different alkyl groups) may be linked to an amino group. This is called **metamersim** (p. 123).

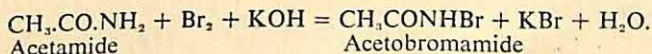
$(\text{CH}_3)_3\text{N}$	$\text{CH}_3\text{CH}_2\text{NH}\text{CH}_3$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$
Trimethylamine	Methylethylamine	<i>n</i> -Propylamine
(Tertiary amine)	(Secondary amine)	(Primary amine)

The primary amines.—The simplest are methyl- and ethyl-amines, the typical representatives of the series. **Methylamine**, CH_3NH_2 , occurs in brine in which herring has been salted, and also in the decomposition products of alkaloids and proteins. It is a refrigerant.

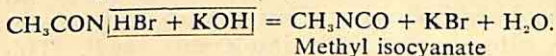
Preparation.—(1) Methylamine may be prepared by boiling methyl isocyanate with caustic potash. The amine escapes as a gas. Wurtz (1817-84) discovered the method in 1848.



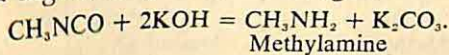
(2) *Hofmann reaction.*—Methylamine is conveniently made by reacting acetamide with bromine and excess of caustic potash (p. 166). Equivalent amounts of bromine and acetamide are mixed together and KOH solution (10%) is slowly added until the colour due to bromine disappears. Acetobromamide is thus formed:



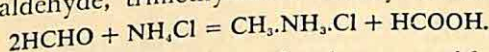
This, on warming with an excess of strong KOH solution, loses HBr and yields methyl isocyanate by intramolecular rearrangement, pot. bromamide, CH_3CONKBr , being an unstable intermediate product.



The isocyanate by alkaline hydrolysis gives methylamine which is absorbed in dilute HCl. The yield is about 90%. One C atom has been eliminated from the amide during the process. This is useful in passing from a higher to a lower homologue.

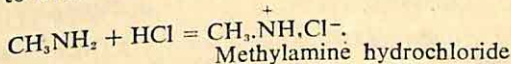


(3) Methylamine is also made by heating a mixture of formalin and ammonium chloride to 104° . At higher temperature and with solid paraformaldehyde, trimethylamine chiefly results.

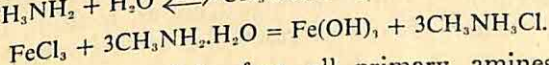
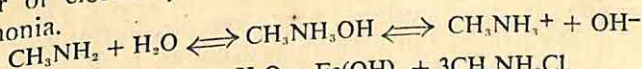


Properties.—Methylamine is a colourless gas with an ammoniacal but fishy odour. Unlike ammonia, it burns in air with a yellow flame. It is highly soluble in alcohol and water; the aqueous solution is alkaline to litmus.

Reactions.—(1) Methylamine, like ammonia, readily forms white fumes with HCl due to salt formation; the valency of nitrogen thus increases from three to five, the fifth being polar.

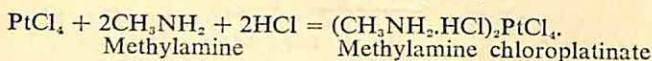


(2) In water it behaves like ammonium hydroxide, forming methylammonium hydroxide which is unstable. The aqueous solution which is alkaline, precipitates metallic hydroxides and is a conductor of electricity; methylamine, therefore, ionises in solution like ammonia.

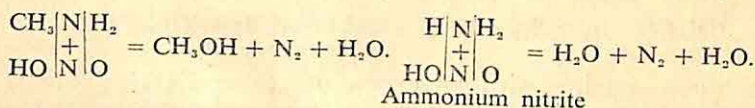


(3) Methylamine and in fact, all primary amines, form double salts with chlorides of gold, platinum and mercury in presence of

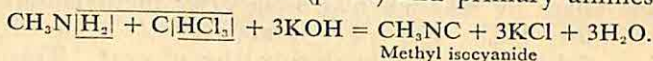
HCl. These are sparingly soluble in water and on ignition, give the metal. The platinum salts are used for the estimation of amines and the determination of their molecular weights (p. 29).



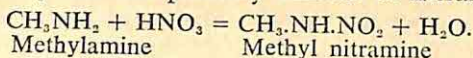
(4) Primary amines and nitrous acid yield alcohol and nitrogen (cf., action of nitrous acid on ammonia, and also on acetamide, p. 166). Methylamine, however, forms mainly methyl nitrite (a gas which readily escapes) and only a little methyl alcohol. Ethylamine gives 60% ethyl alcohol. But secondary and tertiary amines behave differently.



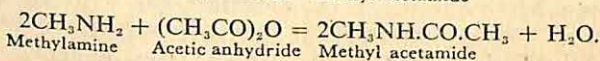
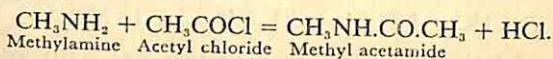
(5) Primary amines react with chloroform (also with bromoform or iodoform) and alcoholic potash on heating to produce carbylamines or isocyanides with characteristic, intolerable smell. This serves as a delicate test both for chloroform (p. 79) and primary amines.



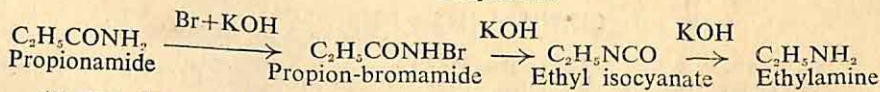
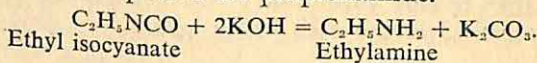
(6) Conc. HNO_3 oxidises primary amines to nitramines:



(7) Methylamine reacts with acid chlorides or anhydrides, producing substituted amides. These are sharp-melting crystals, useful for the identification of amines.



Ethylamine, $\text{C}_2\text{H}_5\text{NH}_2$, may be prepared, like methylamine, by hydrolysing ethyl isocyanate with caustic potash, or by the action of bromine and caustic potash on propionamide.

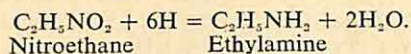


(2) Ethylene and ammonia, NH_3 , combine under pressure at about 400° in presence of cobalt catalyst to yield ethylamine and diethylamine. It is a commercial method.

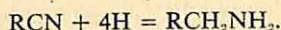
Ethylamine is a colourless, very volatile, inflammable liquid (b.p. 19°). It has a fishy but ammoniacal odour, a biting taste and is highly soluble in water. It closely resembles methylamine.

General methods of preparation of primary amines.—(1) Nitro-paraffins, on reduction with tin and hydrochloric acid, or hydrogen

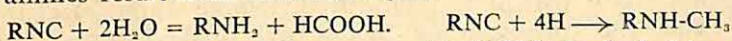
and a nickel catalyst, readily yield primary amines (p. 174). Milder reducing agents *e.g.*, zinc dust and water, give alkylhydroxylamine, R.NH.OH .



(2) Alkyl cyanides, when reduced with sodium and alcohol, give primary amines (**Mendius' reaction**). The yield is poor with tin and HCl ; best results are obtained with lithium-aluminium hydride, LiAlH_4 .

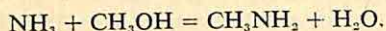


(3) Hydrolysis of alkyl isocyanides gives primary amines; secondary amines result from their reduction.



(4) By boiling alkyl isocyanates with KOH (hydrolysis), primary amines are obtained (p. 203). But isocyanates are difficult to make.

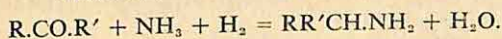
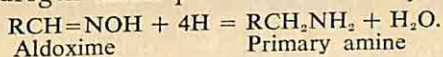
(5) On passing alcohol vapour and ammonia over gently heated thoria.



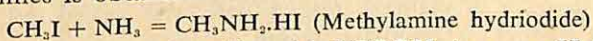
(6) Amides of fatty acids react with bromine and KOH , to give primary amines (p. 203). The amides are catalytically reduced to amines:



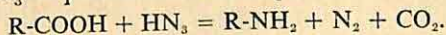
(7) Oximes from aldehydes and ketones, on reduction with sodium amalgam and acetic acid, or with hydrogen in presence of platinum or palladium, form primary amines in good yield. Amines are obtained directly from aldehydes or ketones by passing its vapour with excess ammonia and hydrogen under pressure over Raney nickel at $40\text{--}150^\circ$.



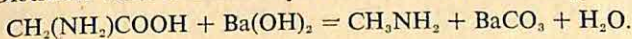
(8) Alkyl halides, when heated to 100° in a sealed tube with alcoholic ammonia, give alkyl amines (Hofmann's method). But the reaction proceeds further and secondary and tertiary amines, together with quaternary ammonium compounds, also result. With anhydrous liquid ammonia at 0° in place of alcoholic ammonia, a better yield of primary amines is obtained.



(9) By reacting a carboxylic acid, RCOOH , in conc. H_2SO_4 solution with hydrazoic acid, HN_3 , in chloroform or benzene at room temp. The free amine is obtained on making the reaction mixture alkaline with NaOH . HN_3 is poisonous and explosive.



(10) Distilled with barium hydroxide, amino-acids give amines:

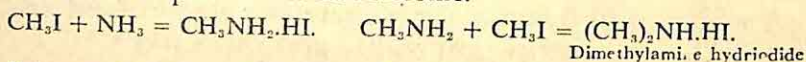


Properties of primary amines.—The first two members are gases; with increase in mol. wt. amines become liquids and then

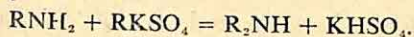
solids. Methyl- and ethylamine are highly soluble in water; the solubility decreases with rise in mol. wt. and the higher amines are insoluble. The lower members have a faintly ammoniacal smell but the higher ones are practically odourless. Chemically, all behave like methylamine. They liberate nitrogen with nitrous acid, combine with acids to form crystalline salts which are soluble in water, give acyl derivatives with acetyl chloride or acetic anhydride, and double salts with PtCl_4 in presence of HCl . Aliphatic amines are somewhat stronger bases than ammonia; thus in water the dissociation constant, k , of ammonia is 1.75×10^{-5} (at 18°) while that of methylamine is 5.00×10^{-4} (at 25°) and k for ethylamine is 5.6×10^{-4} (at 25°), the corresponding pK values are 4.76, 3.30 and 3.25. Unexpectedly, trimethylamine ($k = 6.3 \times 10^{-5}$) and triethylamine ($k = 4.4 \times 10^{-4}$) are weaker than the corresponding mono- and di-alkylamines. Amines combine with picric acid, $(\text{NO}_2)_3\text{C}_6\text{H}_2\text{OH}$, giving crystalline picrates, $\text{B}(\text{NO}_2)_3\text{C}_6\text{H}_2\text{OH}$, where B is a monoacidic base. These have sharp melting or decomposition points, and are useful in the identification of amines. Strong, alkaline oxidising agents *e.g.*, KMnO_4 and NaOH , convert primary amines into ammonia and aldehydes, acids or ketones depending upon the position of the amino group in the chain.

The secondary amines.—The simplest, dimethylamine, $(\text{CH}_3)_2\text{NH}$, occurs in small amounts in pyroligneous acid (p. 85) and also in herring-brine.

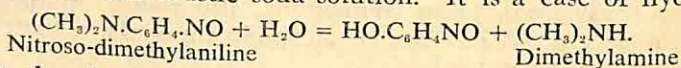
Preparation.—(1) Methyl iodide, heated with alcoholic ammonia in a sealed tube, yields dimethylamine. Primary and tertiary amines are also simultaneously formed together with quaternary ammonium compound. Their separation is troublesome.



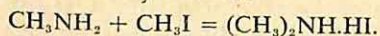
(2) Primary amines, when heated with alkyl potassium sulphate, pass on to secondary amines:



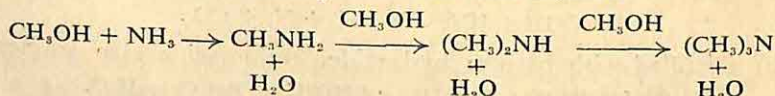
(3) Pure dimethylamine may be prepared by heating nitroso-dimethylaniline with caustic soda solution. It is a case of hydrolysis:



(4) By heating a primary amine with the calculated amount of alkyl iodide, we get a secondary amine:



(5) It is manufactured by passing methanol and NH_3 over Al_2O_3 at 400° ; mono- and tri-methylamine are also formed.

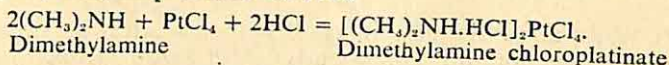


(6) By reducing alkyl isocyanides:



Properties.—Dimethylamine, a gas, can be condensed to a colourless liquid (b.p. 7°). It is basic in aqueous solution and reacts with acids forming crystalline salts, soluble in water.

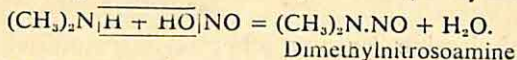
(1) It forms, like methylamine, complex salts with chlorides of platinum, gold, etc., in presence of HCl.



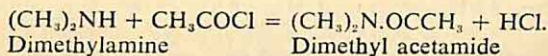
(2) Heated with sodium, it (also methylamine) forms a salt:



(3) Dimethylamine, and in fact, all secondary amines, react with nitrous acid to give nitroso-amine (*cf.*, primary amines, p. 204). *No nitrogen is evolved.* It is a yellow oil (b.p. 177°), volatile in steam. On boiling with HCl, it gives back dimethylamine (as hydrochloride).



(4) Acetyl chloride or acetic anhydride forms acyl derivatives with secondary amines as with primary. Unlike the latter, secondary amines do not give isocyanide with chloroform and KOH (p. 204). They can, therefore, be easily distinguished from the primary.



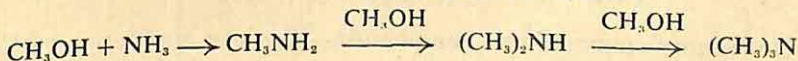
Dimethylamine is used widely in making herbicides and dimethylformamide (a solvent for spinning acrylic fibres) and as also an accelerator for vulcanization of rubber.

The tertiary amines.—The simplest, trimethylamine, $(\text{CH}_3)_3\text{N}$, is present in the distillate of the residue, left after fermentation of the beet-sugar molasses, in some plants, and also in the excreta of fish.

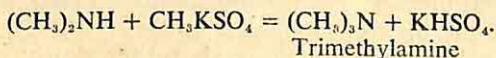
Preparation.—(1) Heated in a sealed tube, methyl iodide and alcoholic ammonia form trimethylamine along with mono- and di-



(2) Trimethylamine is manufactured by heating ammonium chloride with a large excess of dry formaldehyde in an autoclave between 120 - 160° , or passing methanol and ammonia over alumina at 400°

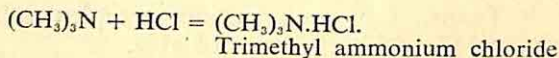


(3) Secondary or primary amines when heated with alkyl potassium sulphate, pass on to tertiary amines.

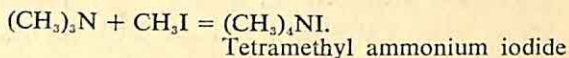


(4) Pure tertiary amines are, however, conveniently obtained by heating quaternary ammonium hydroxides (p. 209).

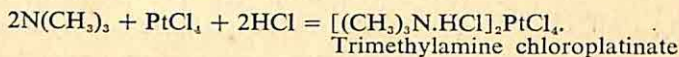
Properties.—Trimethylamine is a colourless gas, highly soluble in water, and has a fishy, ammoniacal odour. It resembles methylamine in some respects. (1) It forms salts with acids.



(2) With alkyl halides, it readily forms additive products called quaternary ammonium compounds (*difference from primary and secondary amines*).

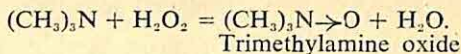


(3) Like primary and secondary, tertiary amines form complex salts with PtCl_4 in presence of HCl .



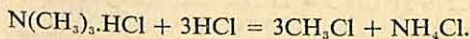
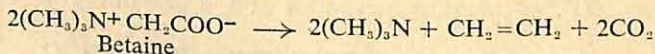
(4) Trimethylamine (or any other tertiary amine) does not react with HNO_2 (except forming the salt, $(\text{CH}_3)_3\text{N} \cdot \text{HNO}_2$), or with acid chlorides. Nor does it give the isocyanide reaction. Tertiary amines can thus be distinguished from the primary and secondary.

(5) A tertiary amine forms with aqueous H_2O_2 an *amine oxide*. Trimethylamine oxide occurs in the muscles of the octopus and the dog-fish.



The lower amine oxides are crystalline solids; $(\text{CH}_3)_3\text{NO} \cdot 2\text{H}_2\text{O}$ melts at 98° . These oxides are basic and form salts which are structurally similar to ammonium salts. Trimethylamine-oxide hydrochloride is $[(\text{CH}_3)_3\text{NOH}]^+\text{Cl}^-$; the structure, $(\text{CH}_3)_3\text{N}=\text{O}$ is untenable as the electronic configuration would require 10 electrons in the outer shell of N in place of 8 (*cf.*, p. 37).

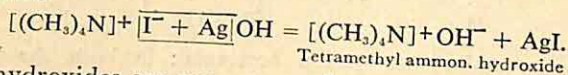
Triethylamine, $(\text{C}_2\text{H}_5)_3\text{N}$, is an oily liquid (b.p. 89°). It is used as an insect attractant and as a warning agent in compressed gases. Choline chloride, used in animal feeds, is made from trimethylamine. Trimethylamine is manufactured by the destructive distillation of beet-sugar molasses which contains betaine. Methyl chloride is made from trimethylamine by heating under pressure with HCl .



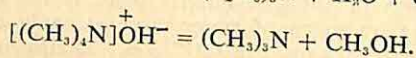
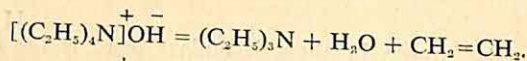
Quaternary ammonium compounds.—Tertiary amines combine with alkyl halides to form quaternary (*quater*, four times) ammonium compounds. For example, trimethylamine and methyl iodide, on warming, give tetramethyl ammonium iodide. They are also formed when a large excess of alkyl iodide is heated with alcoholic ammonia in a sealed tube. The reaction proceeds rather slowly in hydrocarbons or ethers as solvent but much more quickly in alcohols or ketones.



The quaternary ammonium compounds are neutral, colourless and crystalline. They are readily soluble in water and closely resemble the ammonium salts. They are not decomposed by boiling aqueous caustic alkalis (*difference from ammonium salts*); but alcoholic caustic potash decomposes them. Quaternary ammonium compounds are finishing agents in the textile industry. The iodides decompose, on strongly heating, into a tertiary amine and alkyl iodide: $\text{NR}_4\text{I} \rightleftharpoons \text{NR}_3 + \text{RI}$. With moist silver oxide, a quaternary ammonium hydroxide is formed from the iodide. It is a deliquescent, crystalline solid.



These hydroxides are very strong bases—almost as strong as caustic alkalis. They liberate ammonia from ammonium salts, form salts with acids, and absorb carbon dioxide from the air to give carbonates. They decompose, when heated, into tertiary amines, water and an olefine. Tetramethyl ammonium hydroxide, however, splits into trimethylamine and methanol at about 135° .



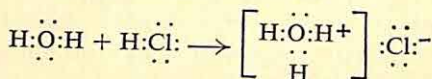
Identification of amines

Reagent	Primary amine	Secondary amine	Tertiary amine
Chloroform and alc. KOH	Carbylamine formed	No reaction	No reaction
Nitrous acid	Nitrogen evolved	Oily nitrosoamine formed	Forms the nitrite salt
Acetyl chloride or acetic anhydride	Forms amide	Forms amide	No reaction
Platinum chloride and HCl	Forms complex salt	Forms complex salt	Forms complex salt
Methyl iodide at ordinary pressure	No reaction	No reaction	Forms tetra-alkyl ammon. iodide

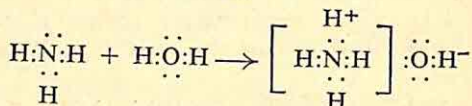
Quaternary ammonium salts may be distinguished by their neutral reaction towards litmus and inability to react with any of these reagents.

Basic nature of amines.—An acid is generally defined as a substance that gives hydrogen ions, and a base as one yielding hydroxyl ions, in aqueous solution. Difficulties, however, arise with non-aqueous solvents, and an acid is now more appropriately defined as a compound having a tendency to lose a proton, and a base as one that has a tendency to gain a proton. When an acid reacts

with a base, a proton is transferred from one base to another. HCl dissolves in water with the transfer of a proton from the chloride ion (a weak base) to the water molecule (a relatively stronger base) as



Similarly, NH_3 dissolves in water as



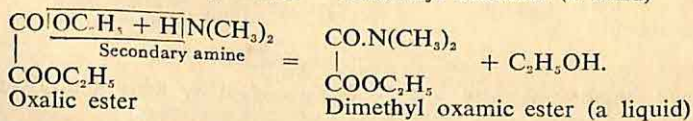
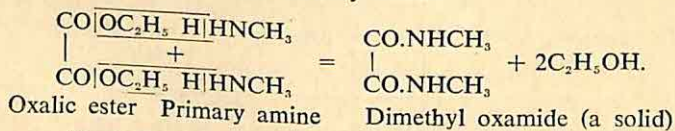
Like ammonia, amines are proton acceptors; in both, the lone electron pair in nitrogen readily attracts a proton and endows the molecule with basic properties. Both NH_3 and aliphatic amines of low mol. wt. easily dissolve in water; the aqueous solution has only a small proportion of OH^- ions; they are weak bases. A high proportion of undissociated molecules occurs in the

solution; solvation takes place by hydrogen bonding as $\text{R}-\overset{\text{H}}{\underset{\text{H}}{\text{N}}} \cdots \text{HOH}$. The

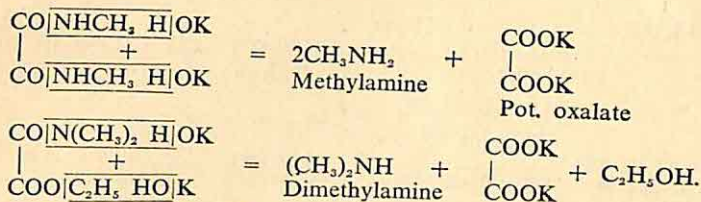
electron-releasing alkyl groups in aliphatic amines increase the electron density on the N which attracts the hydrogen of water more strongly on its unshared electron pair and helps the escape of the OH^- ion. Methylamine is thus a stronger base than ammonia and dimethylamine stronger than methylamine. Tetra-alkyl ammonium hydroxides such as $[(\text{CH}_3)_4\text{N}]^+\text{OH}^-$ have no hydrogen attached to nitrogen; hydrogen bonding and solvation are not possible. They completely ionise and behave like strong bases. A tertiary amine e.g., $(\text{CH}_3)_3\text{N}$, is a very weak base compared with the strong electrolyte, $[(\text{CH}_3)_4\text{N}]^+\text{OH}^-$, as its ionisation in water is quite small, mainly due to hydrogen bonding, $(\text{CH}_3)_3\text{N} \cdots \text{HOH}$.

Separation of the amines and quaternary ammonium compounds from a mixture.—The mixture, containing primary, secondary and tertiary amines as well as quaternary ammonium salts, is first distilled with an excess of KOH, when all the three amines distil over except the non-volatile quaternary compound. The distillate contains the three amines; they can be separated in two ways, viz. Hofmann's and Hinsberg's methods.

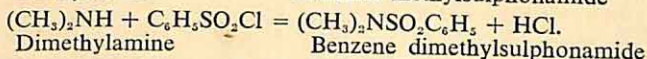
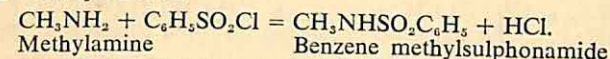
(1) **Hofmann's method.**—The mixture is treated with ethyl oxalate which forms a solid amide with the primary amine, a liquid ester with the secondary, but does not react with the tertiary amine.



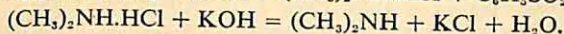
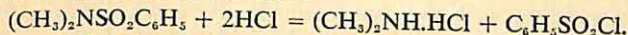
Gaseous amines are passed into ethyl oxalate directly. The mixture is distilled when the tertiary amine, having the lowest b.p., distils over. From the residue, solid oxamide is filtered off. Both oxamide and oxamic ester are then separately treated with KOH solution and the respective amines recovered by distillation.



(2) **Hinsberg's method.**—The mixture of amines is treated with benzene-sulphonic chloride, $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$, with which the primary and secondary amines react, but not the tertiary. The derivative from the primary amine is acidic and readily soluble in aqueous NaOH, that from the secondary is neutral and insoluble. The method is, therefore, used also to distinguish between primary, secondary and tertiary amines.



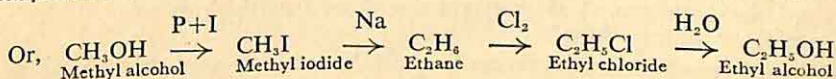
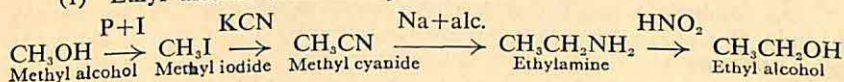
The whole mass is treated with 10% KOH and shaken with ether. The ethereal layer, containing the tertiary amine and the sulphonic derivative of the secondary amine, is removed (the sulphonic derivative of the primary amine remains dissolved in aqueous alkali). On distillation, the tertiary amine is obtained. The liquid in the flask is treated with HCl and distilled with KOH, when the secondary amine is recovered.



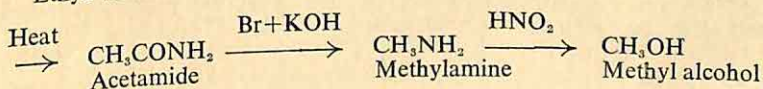
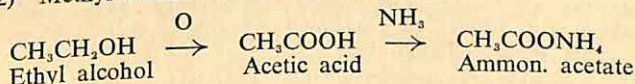
The aqueous layer is similarly treated with HCl, and then distilled with KOH, when the primary amine is obtained. Some secondary sulphonamides being soluble in water, the method is not general. In the modified method, Hinsberg recommends β -anthraquinone-sulphonic chloride instead of benzene-sulphonic chloride. With the highly efficient modern methods of fractionation, separation of the amines is no longer difficult.

Descent and ascent in a homologous series.—It is possible to convert, through intermediate formation of amines, an alcohol or a fatty acid into a higher homologue and vice versa. These are only of academic interest.

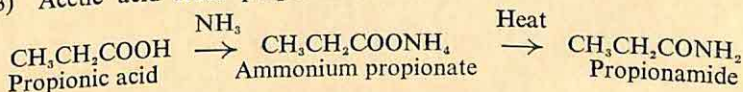
(1) Ethyl alcohol from methyl alcohol :

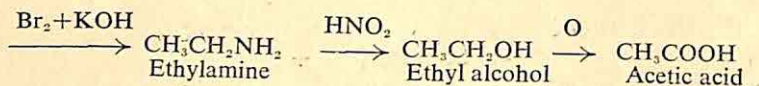


(2) Methyl alcohol from ethyl alcohol :

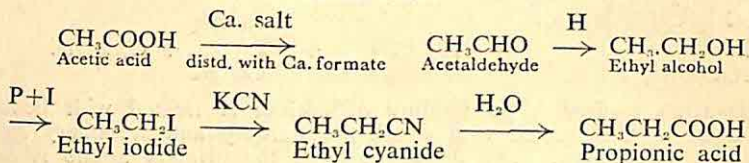


(3) Acetic acid from propionic acid :

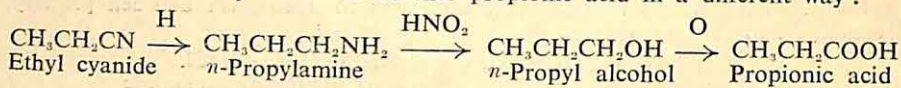




(4) Propionic acid from acetic acid :



The cyanide may be converted into propionic acid in a different way :



QUESTIONS

1. By what reactions can you distinguish primary, secondary and tertiary amines? B.Sc. Pass, 1932, Dacca Uni. (1939, Calcutta Uni.).
2. What are amines? How are the aliphatic primary, secondary and tertiary amines usually separated from a mixture? B.Sc. Pass, 1933, Allahabad Uni.
3. Starting from methyl alcohol, explain illustrating your answer by equations, how acetic acid can be obtained. How can acetic acid be reconverted into methyl alcohol? B.Sc. Pass, 1932, Allahabad Uni.
4. Describe briefly Hofmann's method of preparing the aliphatic amines and state their properties and reactions. How would you distinguish between primary, secondary and tertiary amines? B.Sc. Pass, 1930, Calcutta Uni.; B.Sc. 1951, Gauhati Uni.
5. Describe briefly the methods which you would employ to determine the mode of combination of the nitrogen atom in a substance having the molecular formula, $\text{C}_3\text{H}_9\text{N}$. B.Sc. Pass, 1935, Calcutta Uni.
6. What is an amine? How would you prepare mono-, di- and triethylamine, and also tetraethyl ammonium hydroxide in the pure state? State their properties and uses. B.Sc. Pass, 1936, Calcutta Uni.
7. An aliphatic mono-amine has a vapour density of 36; on heating with excess of CH_3I it gives a quaternary salt having 55.5% I_2 . What is its probable structure?
8. How can you obtain methylamine from formaldehyde, methyl alcohol, acetamide or nitromethane?
9. Discuss the general properties of the amines and show how they resemble ammonia.
10. What are the amines? How would you classify them? What are the various methods of their preparation? Indicate their characteristic reactions. B.Sc., 1946, Benares Hindu Uni.
11. How are amines prepared? Give their chemical properties. How do you distinguish the various kinds of amines? B.Sc. 1941, Agra Uni.

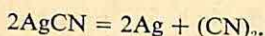
CHAPTER XIX

THE CYANOGEN COMPOUNDS

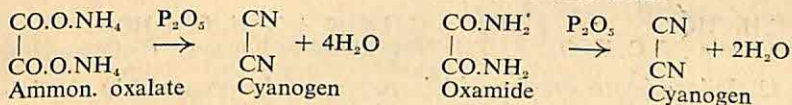
Organic cyanogen compounds are important for various syntheses. The $-C\equiv N$ group present therein, is the first 'compound' radical (p. 48) discovered and named by Gay-Lussac in 1815 (*cyanogen* means blue-compound-forming as Prussian blue has the $-CN$ group). Cyanogen behaves as a monovalent element (*cf.*, NH_4^+), apparently resembling halogens. Chemically, however, there is little similarity between the two.

Cl_2	HCl	$NaCl$	$HOCl$	CH_3Cl
$(CN)_2$	HCN	$NaCN$	$HO-CN$	CH_3CN

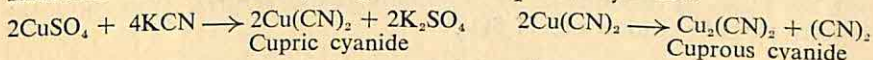
Cyanogen, $(CN)_2$, occurs in traces in blast furnace gases and coal-gas. Gay-Lussac obtained it by heating silver cyanide. Mercuric cyanide behaves similarly and is more convenient to employ; the gas is liberated at a lower temperature if mercuric chloride is mixed with the cyanide.



(2) It may also be obtained by distilling anhydrous ammonium oxalate, or oxamide, $H_2N.CO.CO.NH_2$, with phosphorus pentoxide. It is a case of dehydration. The constitution of cyanogen follows from this mode of formation. It is the nitrile of oxalic acid.

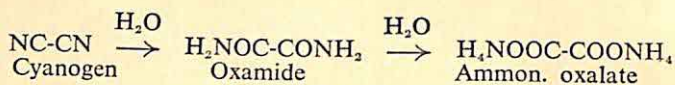


(3) Cyanogen is conveniently made by warming concentrated solutions of copper sulphate and potassium cyanide. Ferric chloride liberates the residual cyanogen from cuprous cyanide.



(4) Cyanogen may be directly made from its elements by sparking carbon electrodes in nitrogen: $2C + N_2 = (CN)_2$.

Properties.—Cyanogen is a colourless, *extremely poisonous* gas with a smell recalling bitter almonds. It can be readily liquefied (b.p. -20.7°). From vapour density, cyanogen is found to be a di-radical, $(CN)_2$; hence the name 'dicyanogen'. It is soluble in 4 vols. of water; the solution decomposes in various ways—ammonium oxalate and carbonate, urea, *azulmic acid*, $C_4H_5ON_5$, etc., being formed. The last one deposits as a brown, amorphous precipitate. Cyanogen burns in air with a violet flame, forming carbon dioxide and nitrogen. On heating to 400° , it forms the polymer, *paracyanogen*, $(CN)_n$, a heavy, brown, non-volatile powder which gives cyanogen at 800° . When treated with aqueous hydrochloric acid, cyanogen is hydrolysed to oxamide and then to ammonium oxalate.

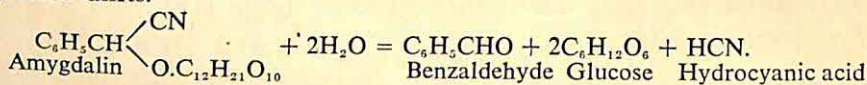


The cyanogen group is hydrolysed to a carboxyl group, a step, generally followed to introduce a carboxyl group into an organic molecule. Passed into a solution of KOH, cyanogen forms potassium cyanide and cyanate like chlorine. A strong solution of caustic potash is, therefore, a good absorbent for the gas.

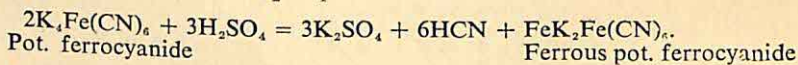


Hydrocyanic acid, HCN, the simplest cyanogen compound, may be regarded as a derivative of methane, three hydrogen atoms of which have been replaced by a trivalent nitrogen. Scheele first obtained it in 1782 by heating Prussian blue with H_2SO_4 , hence the old name *prussic acid*; unaware of its poisonous character, he noted its smell and even its taste. Hydrogen cyanide occurs free in some tropical plants, and in combination with glucose and benzaldehyde, as *amygdalin* in bitter almonds.

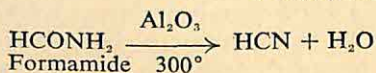
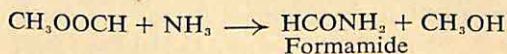
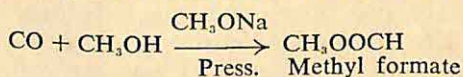
Preparation.—(1) It may be made by hydrolysing amygdalin, $\text{C}_{20}\text{H}_{27}\text{O}_{11}\text{N}$, with dilute H_2SO_4 or *emulsin*, an enzyme, which is present in bitter almonds but in separate cells. On grinding the almonds with water, emulsin and amygdalin (Greek *amygdale*, almond) come in contact and hydrolysis takes place. In amygdalin, benzaldehyde cyanhydrin, $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CN}$, is coupled with two glucose units.



(2) Dilute hydrocyanic acid is conveniently prepared in the laboratory by distilling potassium cyanide or more commonly, potassium ferrocyanide, with dilute H_2SO_4 in a fume-chamber. A little ferrous sulphate improves the yield. With strong H_2SO_4 , carbon monoxide and no HCN is obtained. It is chiefly manufactured from aqueous sodium cyanide and conc. H_2SO_4 .



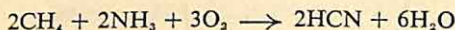
(3) Ammonium formate, or formamide, when heated with P_2O_5 , liberates HCN. Germany makes HCN from carbon monoxide, ammonia and methanol; methanol is recovered and used again.



(4) Hydrocyanic acid is manufactured by leading trimethylamine (from beet-sugar molasses) through a fire-clay tube at 1000° :

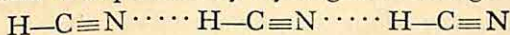


(5) It is also industrially made from ammonia, methane and air, passed over platinum catalyst at about 1500°, or by passing carbon monoxide and ammonia over alumina at 500-700°.

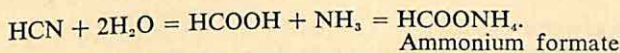


Anhydrous hydrocyanic acid is made by passing pure H_2S over hot mercuric cyanide, $\text{Hg}(\text{CN})_2$, or by treating solid potassium or sodium cyanide with moderately strong H_2SO_4 , the HCN gas evolved is dried by passing through CaCl_2 and then condensed to a liquid by leading to a U-tube cooled by freezing mixture.

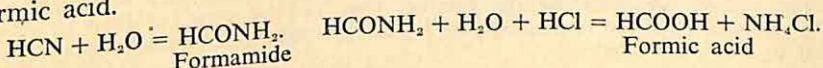
Properties.—Pure hydrocyanic acid is a colourless, highly volatile liquid (b.p. 26°) with an odour resembling that of crushed bitter almonds. It burns with a violet flame and is miscible with water or alcohol in all proportions. Hydrocyanic acid proves fatal to man in *minute* dose (0.05 g.). It inhibits oxidation processes in the cells. The action is so rapid that antidotes (atropine, freshly prepared ferrous hydroxide, hydrogen peroxide, etc.) generally prove futile. It is an extremely weak acid (k at 25° is 7.20×10^{-10}), much weaker than carbonic acid ($k = 3 \times 10^{-7}$ at 18°). The latter, therefore, displaces it from its salts. That is why most metallic cyanides develop an odour of hydrocyanic acid on exposure to moist air. The high dielectric constant of the acid is explained by hydrogen bonding:



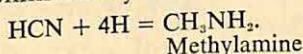
Reactions.—(1) The aqueous acid quickly decomposes, depositing, a brown substance, and the solution contains, among other substances, ammonium formate. Traces of mineral acids retard this decomposition considerably. Anhydrous hydrocyanic acid, however, keeps well for a long time. As HCN yields formic acid on hydrolysis, it is called formonitrile.



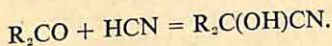
(2) Strong HCl rapidly hydrolyses it to formamide and then to formic acid.



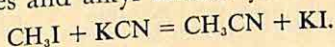
(3) On reduction with sodium amalgam and acetic acid, or hydrogen in presence of colloidal platinum, it yields methylamine (cf., formation of amines from alkyl cyanides, p. 205). Hydrogen and hydrocyanic acid are passed over a metallic cyanide at 200°-300° for making methylamine commercially:



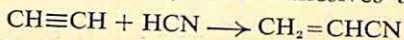
(4) It forms cyanhydrins with most aldehydes and ketones (pp. 128, 138).



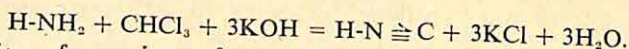
(5) Alkali cyanides and alkyl halides yield alkyl cyanides (p. 74).



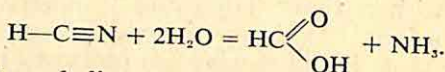
(6) Passed into aqueous Cu_2Cl_2 at 70° , or over a metallic cyanide catalyst at 400° , HCN and acetylene form acrylonitrile, $\text{CH}_2=\text{CHCN}$, used in making synthetic rubber, some adhesives and surface coatings.



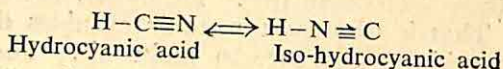
Constitution of hydrocyanic acid.—A primary amine, heated with alcoholic KOH and chloroform, gives an isocyanide (p. 204). Similarly, ammonia gives hydrocyanic acid when heated with chloroform and KOH . From analogy, therefore, hydrocyanic acid is $\text{H}-\text{N}\equiv\text{C}$.



But its formation from ammonium formate, H.COONH_4 , (p. 214) as also its conversion into formic acid on hydrolysis, suggests the structure $\text{H}-\text{C}\equiv\text{N}$.

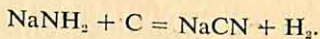
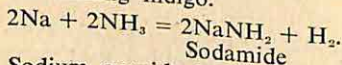


It is, therefore, believed to exist in tautomeric forms which are inseparable due to high interconversion rate. It consists mainly (99.5%) of HCN ; one form gives alkyl cyanides and the other alkyl isocyanides.

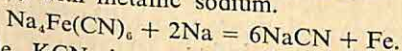


Uses.—Hydrocyanic acid is an important reagent in synthetic chemistry. *In very dilute solution*, it is used in medicine. It is also employed for killing insect pests in fruit-trees which are covered with a cloth tent and sufficient HCN gas introduced. In Bombay, imported cotton is fumigated on the sea with HCN gas for killing boll-weevil. Ships are fumigated with HCN to destroy rats and vermin. Acrylonitrile, and methacrylate and acrylate resins are made from hydrocyanic acid.

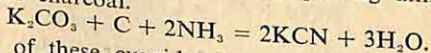
The metallic cyanides.—Cyanides are usually discussed in inorganic chemistry. Of these, sodium and potassium cyanides are the most important. The alkali, alkaline-earth and mercury cyanides are soluble in water, others are only sparingly soluble. Sodium cyanide is made by passing dry ammonia over molten sodium and running the product over red-hot charcoal (800°). About 98% pure NaCN is thus obtained. The intermediate product, sodamide, is used in making indigo.



Sodium cyanide is also obtained by heating sodium ferrocyanide (obtained in coal-gas manufacture) with metallic sodium.



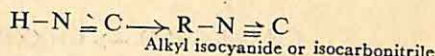
Potassium cyanide, KCN , is prepared by passing ammonia over a heated mixture of K_2CO_3 and charcoal.



Huge quantities of these cyanides are required for the extraction of gold and silver from their ores and also for electroplating. KCN is an important reagent in organic chemistry. Both are terribly poisonous, causing almost instantaneous death even in very minute doses. NaCN and KCN are readily fusible, and highly soluble in water; they are white, crystalline and deliquescent. Their aqueous solution undergoes easy hydrolysis; $\text{NaCN} + \text{H}_2\text{O} \rightleftharpoons \text{NaOH} + \text{HCN}$, and so reacts alkaline. The higher cyanides form complex salts such as ferrocyanides, ferricyanides, cuprocyanides, etc.

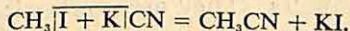
Detection of hydrocyanic acid and cyanides.—(i) On warming a soluble cyanide with HNO_3 and holding a glass rod dipped in AgNO_3 solution in the issuing vapour, the drop at the end of the glass rod becomes turbid—insoluble AgCN being formed. (ii) A solution of HCN , made alkaline with KOH , is boiled with a few drops of FeSO_4 and a drop of FeCl_3 ; on adding sufficient HCl , a precipitate of Prussian blue appears.

Alkyl derivatives of hydrocyanic acid.—When the hydrogen of hydrocyanic acid is replaced by an alkyl group, two types of derivatives are obtained, corresponding to the tautomeric forms of the acid (p. 216), viz., alkyl cyanide and isocyanide. In the first, the alkyl group is attached directly to the carbon of HCN , and in the second, it is linked to the nitrogen:



Alkyl cyanides, $\text{R}-\text{C}\equiv\text{N}$, are also called nitriles of the acids they give on hydrolysis. Thus, methyl cyanide, CH_3CN , is *acetonitrile*. Alkyl cyanides occur in bone-oil.

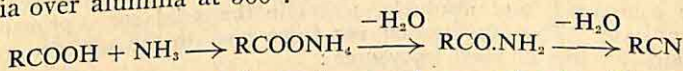
Preparation.—(1) Alkyl halides, when heated with aqueous-alcoholic KCN , form cyanides (p. 74) in good yield. A little isocyanide is also formed, which, unlike the cyanide, is readily hydrolysed by dilute HCl in the cold. Primary halides react most readily, secondary halides poorly and tertiary ones most sluggishly. Alkyl potassium sulphates, dry-distilled with KCN , yield alkyl cyanides with some isocyanide. The carbon chain is lengthened by an additional atom. This is utilised in passing from a lower to a higher member in a homologous series.



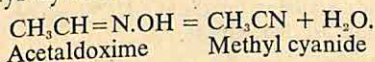
(2) Ammonium salts of fatty acids, or acid amides, when distilled with P_2O_5 , or thionyl chloride, SOCl_2 , form alkyl cyanides (p. 166).



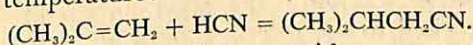
Alkyl cyanides are manufactured by passing a carboxylic acid and ammonia over alumina at 500° .



(3) Aldoximes, on dehydration with acetyl chloride or acetic anhydride, yield alkyl cyanides.

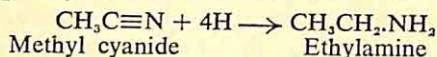


(4) By passing HCN and an unsaturated hydrocarbon over a catalyst at high temperature:

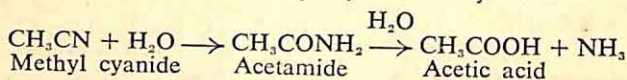


Properties.—The lower alkyl cyanides are colourless, volatile liquids with a strong ethereal odour. They are moderately soluble in water. With increase in molecular weight, however, the solubility decreases, and the density increases; the higher members are crystalline

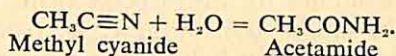
solids. Their reactivity is due to the triple bond. They are less poisonous than hydrogen cyanide. Alkyl cyanides are not true esters as they do not yield alcohol and acid on hydrolysis. On reduction with nascent hydrogen (*e.g.*, sodium and absolute alcohol) alkyl cyanides pass on to primary amines (p. 205). This is analogous to the formation of ethane from acetylene (p. 66) and is called *Mendius' reaction*.



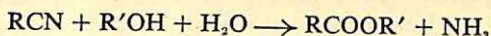
Boiling acids or alkalis hydrolyse the $-\text{CN}$ group to an amide and finally to a carboxyl group; a fatty acid and NH_3 are thus formed. By determining the ammonia, an alkyl cyanide may be estimated.



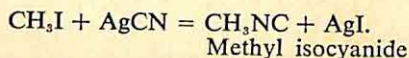
Hydrolysed with 96% H_2SO_4 , or heated with water in a sealed tube at 180° , alkyl cyanides give amides (p. 167; *cf.*, addition of water to acetylene, p. 68). The alkyl group in alkyl cyanides is, therefore, attached to the carbon of $-\text{CN}$.



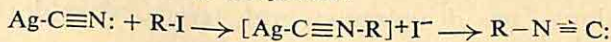
Heated with conc. H_2SO_4 or HCl , an alkyl cyanide and an alcohol form an ester:



Alkyl isocyanides, $\text{R}-\text{N}\equiv\text{C}$, isonitriles or carbylamines are isomeric with alkyl cyanides. They are prepared: (i) by distilling alkyl iodides with silver cyanide, alkyl isocyanides are chiefly obtained:



The difference in the behaviour of KCN and AgCN towards an alkyl halide giving alkyl cyanide and alkyl isocyanide respectively as the main product, is apparently due to the fact that $\text{K}^+[\text{:C}\equiv\text{N:}]^-$, an electrovalent compound, reacts in solution presumably by ionic mechanism. The carbon atom with a lone pair of electrons being more reactive than a similar nitrogen atom, the potential alkyl carbonium ion, R^+ , gets attached to the carbon, giving an alkyl cyanide, $\text{R}-\text{C}\equiv\text{N}$. But $\text{Ag}-\text{C}\equiv\text{N}$: which is a covalent *i.e.*, non-ionic compound, and insoluble, reacts in the solid state, probably in an absorption layer. The alkyl group per force goes to the nitrogen atom with a lone pair, forming an alkyl isocyanide:



In solid state or in non-ionising medium, KCN gives, with an alkyl halide, a much higher proportion of isocyanide.

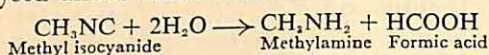
(ii) Alkyl isocyanides, free from cyanides, are obtained by heating primary amines with chloroform and alcoholic caustic potash (p. 79). This is *carbylamine reaction*; the alkyl group in carbylamines or isocyanides is attached to the nitrogen atom (*cf.*, alkyl cyanides, p. 217).

Properties.—The isocyanides are colourless, mobile liquid with *intolerable smell*, by which they may be distinguished from the isomeric cyanides. They are only slightly soluble in water, and more

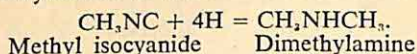
poisonous than alkyl cyanides. Their boiling points are considerably lower than those of the corresponding cyanides:

Methyl cyanide, CH_3CN , b.p. 81.5° . Methyl isocyanide, CH_3NC , b.p. 60° .
Ethyl cyanide, $\text{C}_2\text{H}_5\text{CN}$, b.p. 98° . Ethyl isocyanide, $\text{C}_2\text{H}_5\text{NC}$, b.p. 78° .

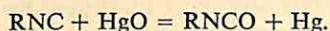
Unlike cyanides, isocyanides are stable towards boiling alkalis. But by dilute mineral acids, they are readily hydrolysed to formic acid and a primary amine at ordinary temperature. Alkyl cyanides are not hydrolysed under these conditions.



Nascent hydrogen reduces isocyanides to secondary amines. The alkyl group in isocyanides is thus attached to the nitrogen.



Mild oxidising agents *e.g.*, mercuric oxide, convert isocyanides to isocyanates:

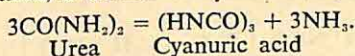


Bromine in the cold, and sulphur at 100° add to the carbon directly:

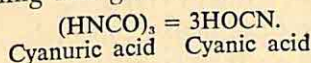


Isocyanides are much more reactive than cyanides due to the lone pair of electrons on the carbon atom. On prolonged heating at about 250° , alkyl isocyanides pass on to the corresponding cyanides: $\text{RNC} \longrightarrow \text{RCN}$.

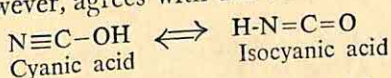
Cyanic acid, HOCN .—On heating dry urea alone, or in a current of chlorine, cyanuric acid, a trimer of cyanic acid, is obtained as crystals.



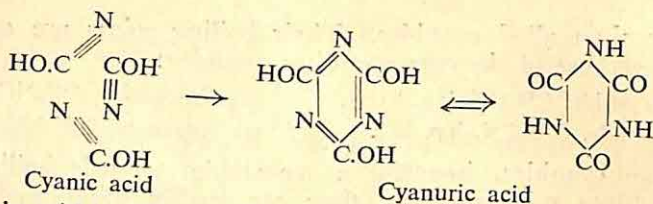
By heating cyanuric acid in a current of carbon dioxide and condensing the vapour in freezing mixture, cyanic acid is obtained as a colourless liquid, smelling like glacial acetic acid.



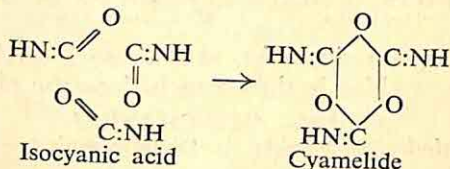
This is a case of de-polymerisation. Cyanic acid is very unstable; above 0° it polymerises mainly into *cyamelide*, a white solid (a second trimer of cyanic acid), and partly into cyanuric acid. On heating, *cyamelide* changes to cyanuric acid. Cyanic acid is rapidly decomposed by water into ammonia and carbon dioxide: $\text{HOCN} + \text{H}_2\text{O} = \text{CO}_2 + \text{NH}_3$. Unlike the acid, its salts are quite stable. *Alkyl cyanates are unknown.* Wöhler obtained urea by heating isomeric ammonium cyanate in 1828 (p. 1). Cyanic acid is believed to exist in tautomeric forms (*cf.*, hydrocyanic acid, p. 216); the tautomerides have not been isolated. The Raman spectrum, however, agrees with the iso-form.



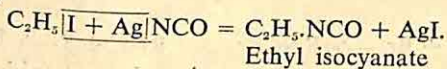
Cyanuric acid has a cyclic structure which may be enolic or ketonic; esters of both (*i.e.*, O-esters and N-esters) are known.



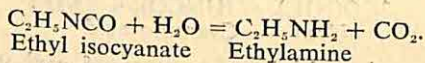
Cyanuric acid is tribasic. Cyamelide, a colourless, non-volatile solid, probably results from the polymerisation of isocyanic acid. Above 200°, it passes over to cyanuric acid.



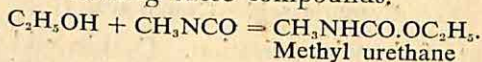
Alkyl isocyanates or **carbimides**, $\text{R}-\text{N}=\text{C}=\text{O}$, were discovered by Wurtz in 1854. They are best obtained by heating alkyl iodides with silver or potassium cyanate, or by the oxidation of isocyanides with HgO (p. 219).



Alkyl isocyanates are intermediate products in Hofmann's method of preparation of amines from amides (p. 203). They are colourless liquids with a suffocating odour. They boil without decomposition. By alkalis, isocyanates are readily hydrolysed to primary amines and carbon dioxide. They do not, therefore, behave as esters which yield alcohol and acid on hydrolysis.



The alkyl group is thus attached to nitrogen and *not* to oxygen. Alkyl isocyanates gradually polymerise to cyanuric esters. They react with alcohols and amines to form crystalline urethanes and alkyl ureas which are useful in detecting these compounds.

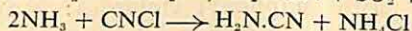
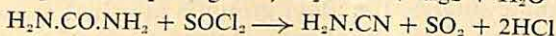


Fulminic acid, $\text{C}\equiv\text{N}-\text{O}-\text{H}$, isomeric with cyanic acid, is unstable and has only been obtained in solution at low temperature. It readily polymerises to its trimer, meta-fulminic acid. Mercury fulminate, $\text{Hg}(\text{ONC})_2 + \frac{1}{2}\text{H}_2\text{O}$, is a detonator (Latin *fulminis*, a thunderbolt). It is obtained by reacting excess of alcohol with a solution of mercury in HNO_3 . Fulminic acid, in aqueous solution, is obtained by the action of mineral acids on fulminates at low temperature. The free acid is a deadly poison and smells like hydrocyanic acid. *Alkyl fulminates are unknown.*

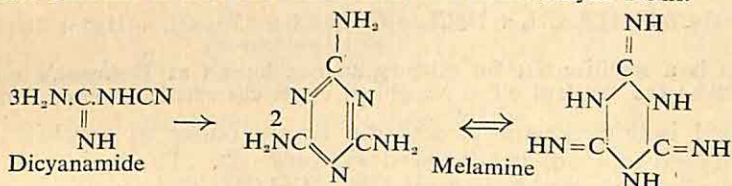
Silver cyanate and silver fulminate are the first example of isomerism (p. 46) discovered by Liebig in 1823; after seven years Berzelius was convinced of such phenomenon and coined the term 'isomerism'.

Cyanamide, NH_2CN , is prepared from aqueous thiourea and freshly precipitated

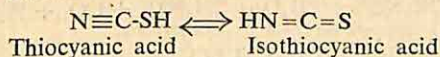
pitated HgO , by heating urea with SOCl_2 , or from cyanogen chloride and ammonia. It is tautomeric: $\text{N}\equiv\text{CNH}_2 \rightleftharpoons \text{HN}:\text{C}:\text{NH}$



It forms colourless crystals (m.p. 42°), soluble in water, alcohol and ether. Calcium cyanamide, $\text{CaN}.\text{CN}$, its most important salt, is a fertiliser and was once a source of urea (p. 266). It is made by passing dry, pure nitrogen over calcium carbide at about 1000° in an electric furnace; CaCl_2 or CaF_2 is added as a flux. $\text{CaC}_2 + \text{N}_2 \rightarrow \text{CaN}.\text{CN} + \text{C}$. Cyanamide in water forms dicyanamide at pH 7-12, which with ammonia and methanol gives **melamine**, a trimer, at 150° . Melamine resins are derived from melamine and formaldehyde; these are more resistant to heat and water than urea-formaldehyde resins.

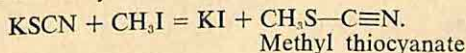


Thiocyanic acid, $\text{N}\equiv\text{C}-\text{SH}$.—Thiocyanic (or sulphocyanic) acid occurs free in onion, and as ammonium salt in coal-gas washings. It may be prepared by adding the calculated amount of dilute sulphuric acid to potassium or barium thiocyanate. It is a pale-yellow liquid with a penetrating smell, miscible with water, ethanol or ether; cooled with ice, it solidifies to a crystalline mass (m.p. 50°). It is very unstable and polymerises readily. Thiocyanic acid is a strong acid, almost as strong as mineral acids. It appears to be tautomeric; salts and esters of both forms are known.

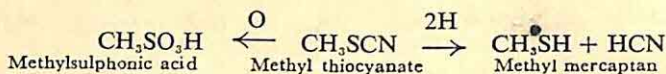


Potassium thiocyanate, KSCN , is made by fusing KCN with sulphur. The fused mass is extracted with alcohol, in which the salt is soluble. The extract, on cooling, gives colourless crystals of the salt. It is used in cotton dyeing and calico printing as a mordant, in medicine to relieve high blood pressure, and also in inorganic analysis. Mercury and ammonium thiocyanates are important. The latter is obtained from the aqueous extract of 'spent oxide' from coal-gas manufacture, and is a delicate reagent for ferric ion. Mercuric thiocyanate, on ignition, puffs up and gives a voluminous, snake-like ash (Pharaoh's serpent).

Alkyl thiocyanates, $\text{R}-\text{S}-\text{C}\equiv\text{N}$, are obtained by heating an alkyl halide with potassium thiocyanate:

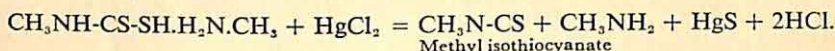
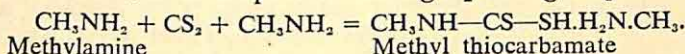


Alkyl thiocyanates are volatile liquids with garlic-like odour, insoluble in water. Their constitution follows from their products of **reduction or oxidation**. With zinc and H_2SO_4 , they yield alkyl hydro-sulphides or **mercaptans**. **Fuming HNO_3** oxidises them to alkyl sulphonic acids:



In alkyl thiocyanates, the alkyl group is attached to sulphur. With chlorine-water, they form sulphonyl chlorides: $\text{R.SCN} + \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{R.SO}_2\text{Cl} + \text{ClCN}$. They partly pass on to isothiocyanates on heating to 180° .

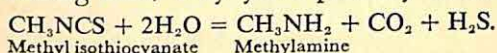
Alkyl isothiocyanates or **mustard oils**, $\text{R-N}=\text{C}=\text{S}$, are obtained by reacting carbon disulphide with primary amines. A dithiocarbamate, first formed, is decomposed with HgCl_2 or AgNO_3 .



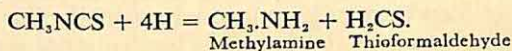
This is a sensitive test for primary amines, known as **Hofmann's mustard oil reaction**; the 'mustard oil' is recognised by its characteristic pungent smell.

Alkyl isothiocyanates possess the strong odour of crushed black mustard seed and are hence called *mustard oils*. The active principle of odour is allyl isothiocyanate, $\text{CH}_2=\text{CH.CH}_2\text{NCS}$, a pungent oily liquid (b.p. 151°). It occurs in the seed as a glucoside, *sinigrin*, which on hydrolysis gives allyl isothiocyanate. During extraction of mustard oil by pressure, some of it passes into the oil. Yellow mustard seed contains *sinalbin* which, on hydrolysis, yields *p*-oxybenzyl isothiocyanate. Any oil, mixed with a little allyl isothiocyanate, smells like mustard oil.

Isothiocyanates are colourless, oily liquids, insoluble in water. On hydrolysis with boiling HCl , they yield primary amines:



On reduction with zinc and H_2SO_4 , they form a primary amine and thio-formaldehyde:



In isothiocyanates, the alkyl group is, therefore, attached to the nitrogen.

QUESTIONS

1. How would you obtain cyanogen in the laboratory? State some of its properties. What is the action of KOH , and boiling HCl upon it?
2. How is hydrocyanic acid prepared? Describe the action of hydrolysing and reducing agents upon HCN .
3. Describe the characteristic reactions of the following groups: $-\text{CN}$, $-\text{CH}_2\text{OH}$, $-\text{NH}_2$, $-\text{OH}$ and $-\text{CHO}$. B.Sc Pass, 1929, Calcutta University.
4. What are 'mustard oils'? Why are they so called? How are they prepared?
5. How would you distinguish methyl cyanide from methyl isocyanide, and ethyl thiocyanate from the isothiocyanate?
6. How can you introduce a $-\text{COOH}$ group into a hydrocarbon? Is it possible to get back the hydrocarbon from the acid formed? If so, how?

CHAPTER XX

THE ALIPHATIC SULPHUR COMPOUNDS

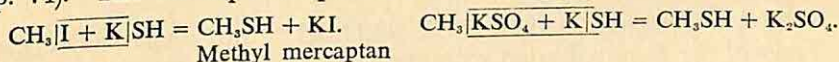
The close analogy between oxygen and sulphur as members of the same group in the periodic table is largely manifested also in organic compounds; we have a series of thio-derivatives (Greek *theios*, sulphur) corresponding to organic compounds containing oxygen:

R—O—H Alcohol	R—O—R Ether	R—CHO Aldehyde	R—CO—R Ketone
R—S—H Thio-alcohol	R—S—R Thio-ether	R—CHS Thio-aldehyde	R—CS—R Thio-ketone, etc.

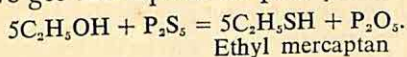
Of these, the thio-alcohols and the thio-ethers are the most important. In their behaviour, especially towards oxidants, they differ from their oxygen analogues.

Thio-alcohols, thiols or mercaptans, R-SH, may be regarded as derived from alcohol by the replacement of oxygen with sulphur, or as derivatives of H_2S , one hydrogen atom of which has been replaced by an alkyl radical. They are also called 'mercaptans', for with great avidity they combine with mercury salts forming mercury mercaptides (*mercurium*, mercury, and *captans*, seizing). They occur in petroleum. The -SH group is called *mercapto* or *sulph-hydryl*.

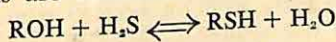
Preparation.—(1) Mercaptans may be prepared by refluxing either alkyl halides or cheaper potassium alkyl sulphates with KSH in alcohol (p. 74). The mercaptan separates on adding water.



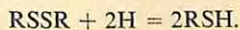
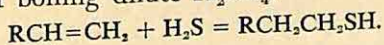
(2) On heating alcohols with phosphorus pentasulphide, P_2S_5 , or trisulphide, P_2S_3 , we get mercaptans in poor yield.



(3) By passing H_2S and alcohol vapour over thorium oxide at $300-350^\circ$, thio-alcohols are obtained.

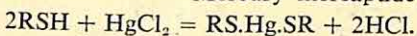
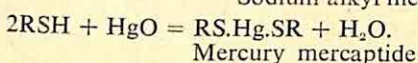
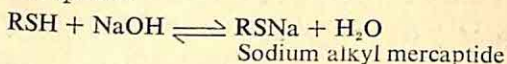


(4) Olefines in liquid phase add up H_2S in ultra-violet light to form thiols; an alkyl disulphide may be reduced to hydrosulphide with zinc dust and boiling dilute H_2SO_4 .

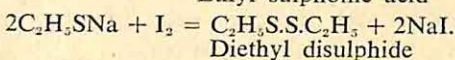
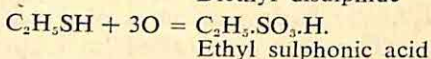


Properties.—The mercaptans are highly volatile liquids (except methyl mercaptan which is a gas) at ordinary temperature. The lower members possess an extremely nauseating odour but the higher ones have rather pleasant smell. Unlike alcohols, they are practically insoluble in water, as they cannot form hydrogen bonds with water. They dissolve in alcohol and ether. The lower members boil at much lower temperature than the corresponding alcohols. The low b.p. and low solubility in water are apparently due to the poor ability of sulphur

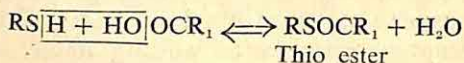
to form hydrogen bonds. The mercaptans behave as weak acids, they are more acidic than alcohols (H_2S is more acidic than H_2O). With aqueous NaOH or KOH , they form salts which are readily hydrolysed by water. Metals can replace the hydrogen in the mercaptans forming mercaptides. Sodium and potassium liberate hydrogen from them as from alcohols (p. 92). With HgO or HgCl_2 , they form insoluble covalent mercury mercaptides



Mercaptans are readily oxidised by air or mild oxidising agents such as H_2O_2 , to disulphides, and by nitric acid or KMnO_4 to sulphonic acids. Iodine and sodium mercaptide give a disulphide which is reduced back to thiol by zinc dust and acid.

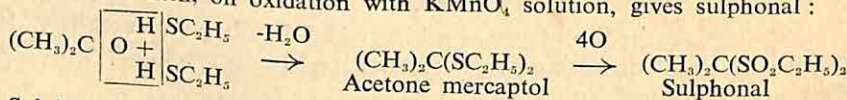


With carboxylic acids, mercaptans, like alcohols, yield ester and water.



Ethyl mercaptan, ethanethiol, $\text{C}_2\text{H}_5\text{SH}$, the most important member of the family, has an extremely disgusting odour, and is simply called 'mercaptan'. It is added to natural gas in U.S.A. for detecting leaks in gas pipes. It is a colourless liquid (b.p. 36°), slightly soluble in water. The foul odour of crude petroleum, mainly due to mercaptans, is largely removed by treating the oil with lead salts, NaOH , CuCl_2 , etc. Thiols are intermediates in the synthesis of vat dyes.

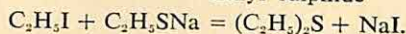
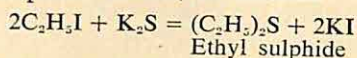
Sulphonal, $(\text{CH}_3)_2\text{C}=(\text{SO}_2\text{C}_2\text{H}_5)_2$.—Acetone condenses with ethyl mercaptan in presence of HCl gas to form acetone mercaptol (cf., formation of acetal, p. 129), which, on oxidation with KMnO_4 solution, gives sulphonal:



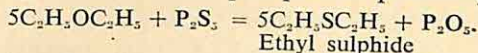
Sulphonal is a colourless, crystalline compound (m.p. 126°), soluble in hot water. It is a sleep-producing drug (soporific). Two other soporifics, *trional*, $(\text{CH}_3)(\text{C}_2\text{H}_5)\text{C}=(\text{SO}_2\text{C}_2\text{H}_5)_2$, and *tetronal*, $(\text{C}_2\text{H}_5)_2\text{C}=(\text{SO}_2\text{C}_2\text{H}_5)_2$, are prepared similarly from methylethyl ketone and diethyl ketone respectively. These are not quite satisfactory as sulphonal for their slow absorption in, and elimination from, the system.

Thio-ethers or **alkyl sulphides**, **R.S.R**, may be regarded as ethers in which the oxygen atom has been replaced by sulphur, or as hydrogen sulphide in which both the hydrogen atoms have been substituted by alkyl groups, same or different.

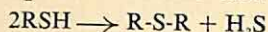
Preparation.—(i) By heating alkyl halides with potassium sulphide or sodium alkyl mercaptide, R.SNa , in alcohol.



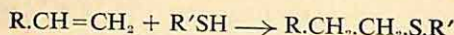
(ii) By heating an ether with phosphorus pentasulphide, P_2S_5 .



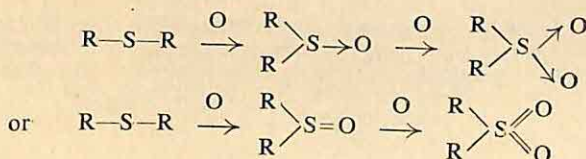
(iii) By passing mercaptans over ZnS and Al_2O_3 at about 300° .



(iv) A thiol adds to an olefine in presence of a peroxide to give a thio-ether:



Properties.—Alkyl sulphides are neutral, volatile liquids, with a disagreeable smell when impure. Pure thioethers have ethereal smell. They boil at higher temperatures than the corresponding mercaptans and ethers, and are insoluble in water. The bivalent sulphur has a tendency to pass over to the tetra- or hexa-valent state. Thus, on mild oxidation (with H_2O_2 in acetic acid at room temp.), thio-ethers yield sulfoxides, R_2SO , and on further oxidation (with boiling KMnO_4 solution), sulphones, R_2SO_2 , are formed. The structures of sulfoxides and sulphones are uncertain; they may have one and two dative bonds according to the octet rule, or only double bonds. Bond length measurement of S-O in these compounds supports the double bond structure.

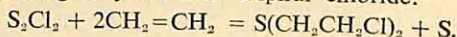


With alkyl halides, alkyl sulphides form sulphonium salts which are stable at ordinary temperature but dissociate on heating. With moist AgO , the latter yield sulphonium hydroxides (cf. quaternary alkyl ammonium compounds, p. 209) which are strong bases.



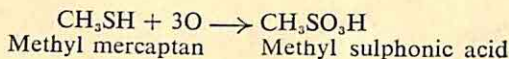
Trialkyl sulphonium hydroxide

'Mustard gas', $\beta\beta'$ -dichloro-diethyl sulphide, $\text{S}(\text{CH}_2\text{CH}_2\text{Cl})_2$, was used as a 'poison gas' in the war of 1914-18 by the Germans and later on, by the allies. It is prepared by passing ethylene into sulphur chloride:

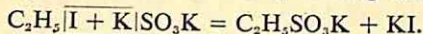


Mustard 'gas' is really a heavy, colourless oily liquid (b.p. 216°), with a faint, mustard-like odour and almost insoluble in water. Its vapours are highly vesicant, producing painful blisters on the skin; it can penetrate rubber and even thick boots. The vapours are, however, absorbed by active charcoal. Bleaching powder or chlorine readily converts mustard gas into its sulphoxide which is harmless. One part in 13000 is fatal if breathed for five minutes. The isomeric $\alpha\alpha'$ -compound, $\text{S}(\text{CH}_3\text{CHCl})_2$, is innocuous.

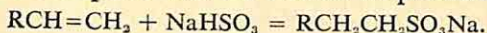
Alkyl sulphonic acids, RSO_3H , are produced from mercaptans by oxidation with strong nitric acid.



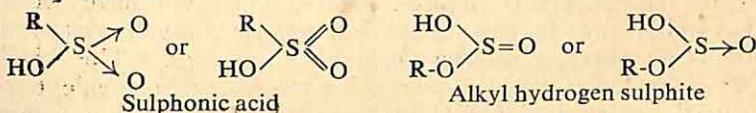
Potassium alkyl sulphonates are formed by heating alkyl halides and K_2SO_3 .



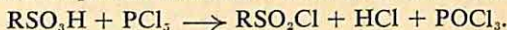
From sodium bisulphite and an olefine in presence of a peroxide:



They may also be obtained from the higher paraffins by the action of fuming H_2SO_4 (p. 50). These are strong, monobasic acids, highly hygroscopic; alkyl sulphonic acids can be reduced back to mercaptans, but are not hydrolysed by alkali. Lower members are thick liquids, higher members are crystalline solids, readily soluble in water. Sulphonic acids and their salts are odourless. In sulphonic acids, sulphur is linked to the carbon atom. They are distinct from the isomeric alkyl hydrogen sulphites which are esters and readily hydrolysed by alkali:



With PCl_5 , the sulphonic acids form sulphonyl chlorides which give esters with alcohols. The sulphonic acids cannot be esterified directly with alcohols.



Alkyl derivatives of phosphorus and arsenic.—Nitrogen, phosphorus and arsenic, members of the same group in the periodic table, form similar alkyl derivatives.

The phosphines.—The hydrogen atoms of phosphine, PH_3 , like those of NH_3 , are replaceable by alkyl groups, and we have primary, RPH_2 , secondary, R_2PH , and tertiary, R_3P , phosphines, as well as quaternary phosphonium compounds, R_4PX . Alkyl phosphines resemble the alkyl amines, but they are less basic and more susceptible to oxidation than the amines. Alkyl phosphines are more basic than PH_3 (cf. amines, p. 206).

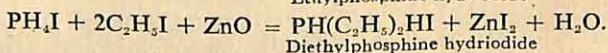
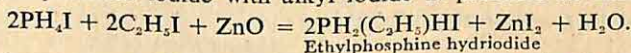
Preparation.—Only tertiary and quaternary compounds are obtained by heating phosphine and an alkyl iodide (cf., formation of amines, p. 205). The latter is soluble in water but not the former, their separation is easy.



Tertiary phosphines result on heating alkyl iodides with phosphonium iodide, or reacting phosphorus trihalide with excess Grignard reagent.

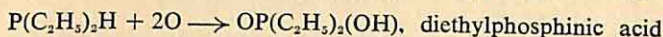
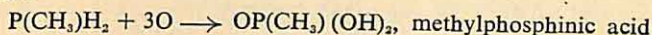


The secondary and primary (but not the tertiary) phosphines are obtained by heating phosphonium iodide with alkyl iodide in presence of zinc oxide.

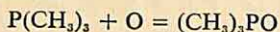


Salts of primary phosphines are readily decomposed by water but not those of other phosphines. Hence a secondary phosphine can be easily separated from the primary

Properties.—Methyl phosphine is a gas (b.p. -14°), but others are colourless liquids with unpleasant odour and a bitter taste. They are sparingly soluble in water, and being feeble bases, do not affect litmus. There is no hydrogen bonding in phosphines; this explains the low b.p. of phosphine and its alkyl derivatives and their slight solubility in water, compared with the corresponding nitrogen derivatives. They form water-soluble salts with acids, and are highly poisonous. The lower members are spontaneously inflammable. Phosphines are readily oxidised by air. Conc. HNO_3 converts primary and secondary phosphines into acids:

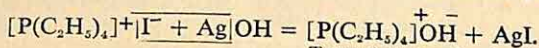


Tertiary phosphines form very stable oxides on exposure to air and also by the action of HNO_3 (cf. amine oxides, p. 208); the oxygen cannot be removed on heating with sodium.

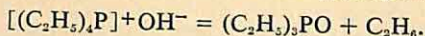


Trimethylphosphine oxide

Quaternary phosphonium compounds, on treatment with moist silver oxide, give corresponding tetra-alkyl phosphonium hydroxides. These are as strong bases as tetra-alkyl ammonium hydroxides, absorbing CO_2 from the air, and giving strongly alkaline aqueous solutions. The base, on heating, splits up into a phosphone oxide and a paraffin (cf., ammonium bases, p. 209).

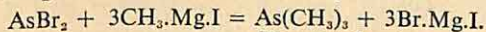


Tetraethyl phosphonium hydroxide

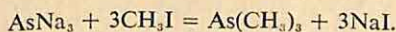


Unlike nitrogen, phosphorus can form a decet in its valency shell and exhibit pentavalency, e.g., R_3PX_2 , PCl_5 , etc. Oxygen compounds of phosphorus, in its highest valence state, may have a double bond between P and one of its O atoms but as these compounds behave more or less like those with a semipolar bond, the bond is possibly intermediate in character; R_5PO , for example, is better represented by $\text{R}_3\text{P} \rightarrow \text{O} \longleftrightarrow \text{R}_3\text{P} = \text{O}$

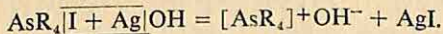
The arsines.—The alkyl derivatives of arsenic are called **arsines**. We have primary, secondary and tertiary arsines as well as quaternary arsonium compounds. The arsines, however, possess no basic property and form no salts; they are insoluble in water. They are colourless liquids (except monomethyl arsine which is a gas), with a stupefying odour and are poisonous. The tertiary arsines are obtained by the action of arsenious halides on excess of Grignard reagent, or by heating sodium arsenide with alkyl iodide:



Trimetnyl arsine



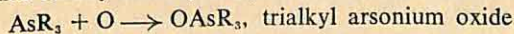
The tertiary arsines form quaternary arsonium compounds with alkyl iodide: $\text{AsR}_3 + \text{RI} = [\text{AsR}_4]^+[\text{I}^-]$ (tetra-alkyl arsonium iodide). These, with moist silver oxide, yield quaternary arsonium hydroxides which are strong bases like similar nitrogen and phosphorus derivatives, and on heating, split up into trialkylarsonoxide and a paraffin.



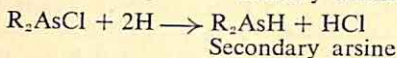
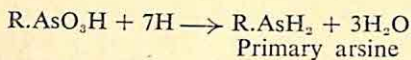
Heat



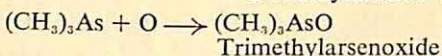
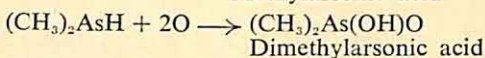
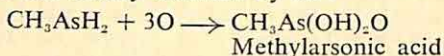
Tertiary arsines readily take up oxygen from the air and form oxides:



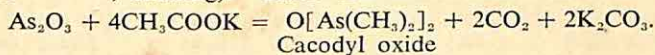
Primary and secondary arsines may be prepared by reducing mono- and di-alkyl arsonic acids, RH_2AsO_3 and R_2HASO_3 , respectively with zinc and sulphuric acid. Dialkylchloroarsine on reduction gives secondary arsine.



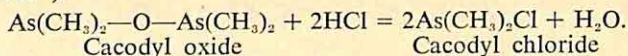
The arsines are readily oxidised by air :



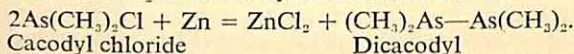
Cacodyl oxide, dimethyl arsenic oxide, $(\text{CH}_3)_2\text{As-O-As}(\text{CH}_3)_2$.—When equal amounts of arsenious oxide and potassium acetate are distilled, a fuming liquid passes over. It is cacodyl oxide, so named by Berzelius for its intolerable smell (Greek *kakodes*, stinking). Cadet thus discovered it in 1760.



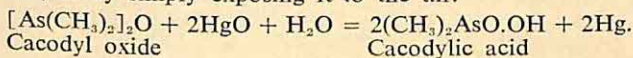
This reaction which is very delicate, is utilised for detecting acetic acid (p. 152) or arsenic. Cacodyl oxide is a liquid (b.p. 150°), insoluble in water, alcohol or ether, and extremely poisonous. It is spontaneously inflammable due to the presence of cacodyl, $\text{As}_2(\text{CH}_3)_4$, as impurity. Cacodyl oxide is a weak base; distilled with HCl, the chloride is obtained; it is an inflammable liquid (b.p. 109°).



Dicacodyl (commonly called cacodyl) is obtained by heating cacodyl chloride with zinc or mercury in an atmosphere of CO_2 (cf., formation of ethane from CH_3I , p. 44). Bunsen isolated cacodyl in 1842 and regarded this complex as 'an organic atom or radical'. Cacodyl is a poisonous liquid (b.p. 170°) with a nauseating smell. It is spontaneously inflammable in air.



Cacodylic acid, $(\text{CH}_3)_2\text{AsO(OH)}$, is obtained by heating cacodyl oxide with HgO and water, or by simply exposing it to the air.



Cacodylic acid is a colourless, odourless and crystalline compound (m.p. 200°), soluble in water. It is a weak acid. Its salts are non-poisonous; the sodium salt is a tonic. When given by the mouth, it imparts the characteristic odour of cacodyl oxide to the breath, sweat and urine.

QUESTIONS

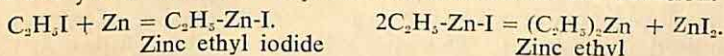
1. What are mercaptans? Why are they so called? How would you prepare ethyl mercaptan? Mention some of its characteristic properties.
2. How is sulphonal prepared? What is it used for?
3. How would you distinguish between ethyl hydrogen sulphite and ethyl sulphonic acid? What is the structural difference between the two?
4. What is cacodyl oxide? How is it prepared? What is 'cacodyl oxide test' for acetates?
5. Illustrate with examples: the alkyl derivatives of nitrogen, arsenic and phosphorus are similar.

CHAPTER XXI

THE ORGANO-METALLIC COMPOUNDS

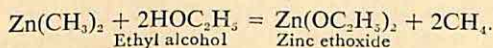
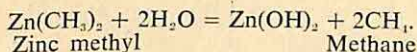
The alkyl derivatives of metals are generally termed *organo-metallic compounds*. Many metals, e.g., Na, Li, Zn, Mg, Sn, Si, Pt, Au, Ag, Pb, etc. form such compounds. Of these, Zn, Mg, Si and Pb alkyls are the most important. They are generally colourless, mobile liquids with low boiling points. Some have pleasant odour and others have foul smell. A few are toxic. Many of them burn violently in air, and are readily decomposed by water, alcohol, etc. Unlike alkyl derivatives of non-metals, organo-metallic compounds are generally very unstable.

Zinc alkyl compounds.—In 1849 Frankland discovered zinc alkyls while attempting to isolate *free radicals* from alkyl halides by removing the halogen with zinc. In 1929 Paneth proved the existence of free methyl radical by the thermal decomposition of tetramethyl lead. Alkyl iodides, warmed with *excess* of freshly made zinc filings or better, with zinc-copper couple (p. 42), produce zinc alkyl iodide (with insufficient zinc, paraffins are formed). When this is distilled in an atmosphere of CO_2 , zinc alkyl, R_2Zn , is obtained. Vacuum distillation improves the yield. A little ethyl acetate accelerates the reaction.



Other zinc alkyls may be similarly prepared. *Zinc methyl*, $\text{Zn}(\text{CH}_3)_2$, is a colourless liquid (b.p. 46°) with repulsive odour and heavier than water (sp. gr. 1.39). It burns spontaneously in air with a reddish flame, forming CO_2 , water and clouds of zinc oxide. *Zinc ethyl*, $\text{Zn}(\text{C}_2\text{H}_5)_2$, is also a colourless, inflammable liquid, (b.p. 118°) with similar properties. Zinc alkyls are corrosive to the skin.

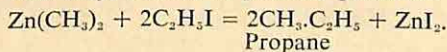
Reactions.—(1) Water and alcohol readily decompose zinc alkyls to paraffins :



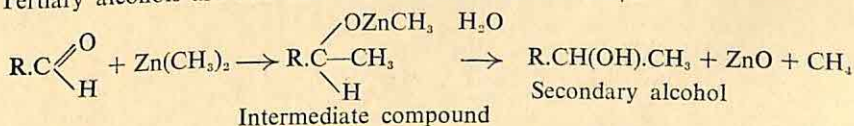
(2) With halogens, they combine energetically yielding alkyl halides :



(3) They react with alkyl iodides to produce paraffins :



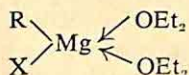
(4) Zinc alkyls and aldehydes interact to produce secondary alcohols. Tertiary alcohols are obtained from ketones and zinc alkyl.



Similarly, zinc alkyl may be used for obtaining ketones and tertiary alcohols by reacting with acid chlorides. For synthetic

purposes, however, they have been practically replaced by more convenient Grignard reagent. But as zinc alkyls react less violently, they are employed if intermediate products are to be isolated.

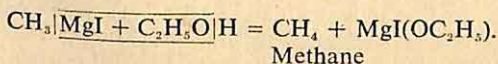
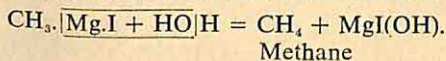
Magnesium alkyl halides were first made by the French chemist, Victor Grignard, in 1900 and are better known as *Grignard reagents*. They have the general formula, $R-Mg-X$, X being a halogen atom and R a hydrocarbon radical, such as ethyl, C_2H_5- , allyl, $CH_2=CH-CH_2-$, phenyl, C_6H_5- , etc. They are prepared and manipulated more easily and conveniently than zinc alkyl halides; they are not spontaneously inflammable. They react with a larger variety of compounds and have proved very useful in organic syntheses in the laboratory. Grignard (1871-1935) won the Nobel prize for this in 1912. The structure of Grignard reagent has not been definitely established; it appears to exist in ethereal solution as an additive complex with ether:



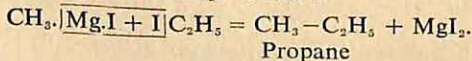
Magnesium methyl iodide, $CH_3.Mg.I$, is prepared by adding scrupulously *dry* and pure methyl iodide (dissolved in dry ether distilled over sodium) to clean and dry magnesium ribbon cut into very small pieces. Tetrahydrofuran or dimethyl ether of ethylene glycol is also used as a solvent. The metal dissolves with evolution of heat, and magnesium methyl iodide formed, remains in solution. By evaporating off the ether in an inert atmosphere, the Grignard reagent may be obtained as a white, crystalline solid, combined with ether. The reagent, however, is not usually isolated but used in ethereal solution directly. It is essential that everything should be *absolutely dry*; even traces of moisture may inhibit the reaction. A trace of iodine helps starting the reaction which, once started, proceeds with increasing speed. Alkyl iodides react more rapidly than bromides and alkyl bromides far more rapidly than chlorides. The longer the alkyl group, the more sluggish the reaction. The yield is generally 85-90%. Magnesium dialkyls, MgR_2 , may be obtained by the action of magnesium on mercury dialkyls. They are not important.

Synthetic uses of Grignard reagent.—(1) Saturated hydrocarbons are produced by reacting with

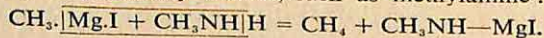
- (i) hydroxy-compounds, such as water or alcohol :



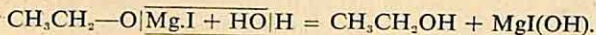
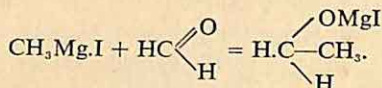
- (ii) alkyl halides, such as ethyl iodide :



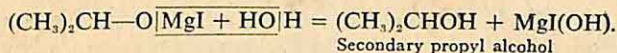
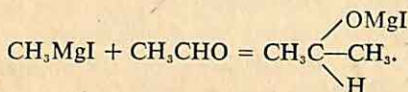
- (iii) primary or secondary amines, such as methylamine :



(2) Primary alcohols are formed by the action of formaldehyde gas on Grignard reagent in ether. The additive compound is hydrolysed with dilute acid.

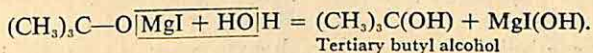


(3) Secondary alcohols are obtained on reacting with aldehydes other than formaldehyde.

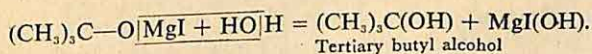
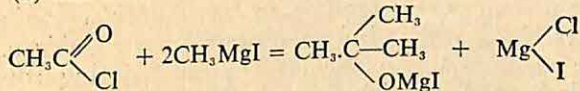


(4) Tertiary alcohols result when Grignard reagent reacts with

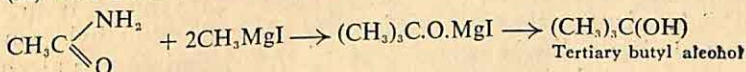
(i) ketones, such as acetone :



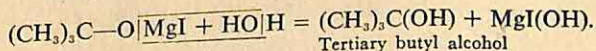
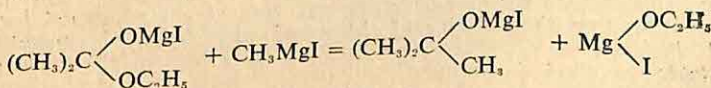
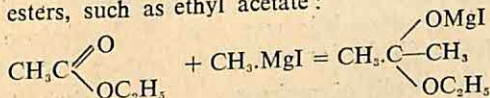
(ii) acid chlorides, such as acetyl chloride :



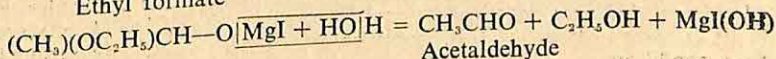
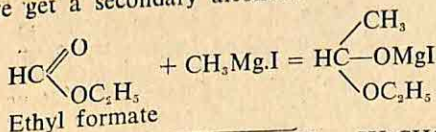
(iii) acid amides, such as acetamide :



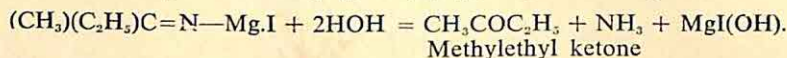
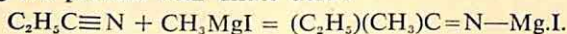
(iv) esters, such as ethyl acetate :



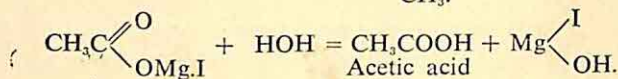
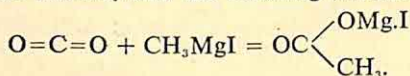
(5) Aldehydes are obtained with ethyl formate ; with excess Grignard reagent, we get a secondary alcohol :



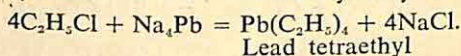
(6) Ketones result on reacting with any alkyl cyanide except methyl cyanide and hydrolysing the product with dilute acid:



(7) Carboxylic acids are formed when Grignard reagent absorbs CO_2 from dry ice (solid carbon dioxide) and the resulting product is hydrolysed with dilute acid.

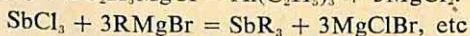
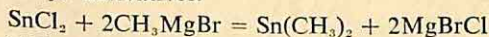


Lead tetraethyl, $Pb(C_2H_5)_4$, is manufactured by passing the hot vapour of ethyl chloride, C_2H_5Cl , under pressure over an alloy of lead and sodium, in finely divided form, in presence of ethylene bromide. It is separated from the reaction mixture by steam distillation. It is soluble in ether and suffers no hydrolysis.

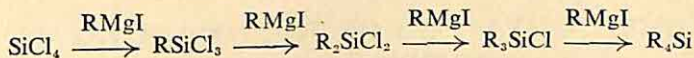


Lead tetraethyl is a colourless, heavy, very poisonous liquid (b.p. 202°) which slowly decomposes in presence of light. In commerce, it is known as 'ethyl' and extensively used as an 'anti-knock' material for petrol in automobiles along with ethylene dibromide, etc. (*vide* p. 54). Ethylene dibromide combines with the PbO , formed during combustion, to produce volatile $PbBr_2$ which accompanies exhaust gases from the cylinders. A very small amount, about 0.1%, is sufficient to prevent the detonation of petrol vapour and air under high compression. Lead tetraethyl is the best anti-knock material known—0.04% of it is as efficient as 25% of benzene. Midgley introduced it in 1922. One U.S.A. plant makes 60 million lb. of lead tetraethyl annually. By electrolysis of a liquid complex of triethyl aluminium and sodium fluoride using lead electrode, tetraethyl lead is obtained at the anode (which collects at the bottom and is removed). Aluminium deposits at the cathode, and ethyl radicals, formed at the anode, react with lead.

Besides these, alkyl compounds of antimony, tin, aluminium, boron, etc., are also sometimes used for various purposes. One common method for their preparation is to treat the chloride of the metal with Grignard reagent when the metal alkyl is formed. The more metallic the nature of the element, the more unstable the alkyl derivatives.



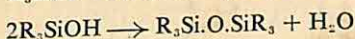
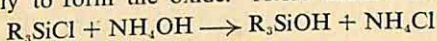
Silicon compounds.—Like carbon silicon is tetravalent in organic compounds; but its maximum covalency being six and nature electro-positive, compounds of silicon behave differently from similar carbon compounds. Alkylsilanes are silicon hydrides (silanes) with one or more hydrogen atoms replaced by alkyl radicals, e.g., methylsilane, CH_3SiH_3 , and tetramethylsilane, $(CH_3)_4Si$. These may be prepared (i) by heating zinc alkyl and silicon tetrachloride in a sealed tube at 160° , or reacting Grignard reagent with $SiCl_4$. A mixture of alkylsilanes is thus obtained; it is, however, possible to have any product by controlling conditions.



They are manufactured by passing vapour of alkyl halide and SiCl_4 over zinc or aluminium at about 400° . Alkylsilanes are colourless oily liquids, unaffected by air, acids or alkalis. Orthosilicates (or ethers), $\text{Si}(\text{OR})_4$, are formed when SiCl_4 and alcohols react; these are volatile liquids with a pleasant odour, readily hydrolysed by water.

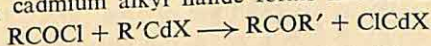


Trialkyl chlorosilanes, R_3SiCl , on hydrolysis with NH_4OH , give *silanol* which loses water readily to form the oxide. Acids cannot esterify silanols.



Diols, $\text{H}_2\text{Si}(\text{OH})_2$, easily polymerise by condensation (with elimination of water) and form *silicones* which are commercially important. Silicone resins are widely used to give protective coating to metal surfaces; methylchlorosilane is employed for water-repelling finishes on cotton fabrics, glass surface, wooden and leather goods, etc. Silicone resins are good electrical insulators.

Cadmium dialkyls, R_2Cd , may be made by reacting alkyl magnesium bromide (Grignard reagent) with anhydrous CdCl_2 . They are volatile liquids, fuming in air; they are much less reactive than magnesium or zinc alkyls. With acid chlorides, cadmium alkyl halide forms ketones in high yield:



Lithium alkyls, prepared by heating an alkyl halide and the metal in an inert solvent such as petrol ether in absence of moisture and oxygen, are covalent compounds (e.g., CH_3Li); they are soluble in organic solvents and usually more reactive than Grignard reagents. Unlike the latter, they add on to the ethylenic double bond; they react more readily with nitriles and also give better yields of ketones. Lithium alkyls are safe and easy to manipulate but are more costly than Grignard reagents.

QUESTIONS

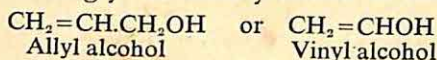
1. How is lead tetraethyl prepared? What is it used for?
2. What is the action of (a) water, (b) alcohol, (c) chlorine, and (d) acetaldehyde on zinc ethyl? Give equations. How would you obtain zinc ethyl?
3. Describe in detail the preparation of Grignard reagent from methyl iodide. How could (a) methane, (b) tri-methyl carbinol and (c) acetic acid be prepared from this reagent? B.Sc., London, 1933.
4. Give a general account of the application of the Grignard reagent in organic syntheses. B.Sc., London, 1932.
5. What are Grignard reagents and how are they prepared? Outline their uses in synthetic organic chemistry. B.Sc., Degree Exam. 1942, Andhra University; B.Sc., 1941, Benaras Hindu University.
6. How would you prepare a Grignard reagent? What is the constitution of the substance? State in brief outline how it can be used in synthesising different types of compounds. B.A., Degree Exam. 1941, Madras Uni.; B.Sc. Pass, 1951, Rajasthan Uni.
7. A compound has 64.86% C and 13.51% H. It can be prepared from acetyl chloride and zinc methyl. What is its structural formula?

CHAPTER XXII

SOME DERIVATIVES OF THE UNSATURATED HYDROCARBONS

When $-OH$, $-COOH$, $-NH_2$, etc. groups enter into a paraffin molecule, we have alcohols, acids, amines, etc.—all saturated compounds. When they occur in the olefines and the acetylenes, unsaturated alcohols, acids, etc. result. These naturally have dual functions, as an olefine (or an acetylene) and as an alcohol (or aldehyde, etc.).

Unsaturated alcohols may have the hydroxyl group attached to a carbon which is singly- or doubly-linked to another, e.g.,

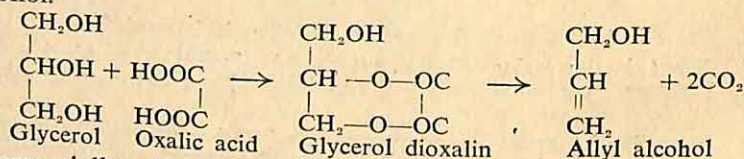


The simplest member *viz.*, vinyl alcohol, is unknown in the free state, the $>C=CHOH$ group being unstable. Attempts to obtain vinyl alcohol result in acetaldehyde which is its keto form. Vinyl alcohol apparently exists in equilibrium with acetaldehyde as keto-

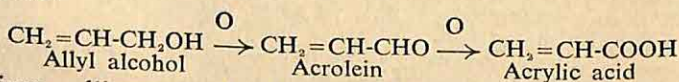
enol tautomers: $CH_2=CHOH \rightleftharpoons CH_3C \begin{array}{c} O \\ // \\ H \end{array}$ The enolic form of

aceto-acetic ester (p. 198) is an example of this type. From the mixture, vinyl alcohol has been isolated as a mercury oxychloride derivative. Vinyl bromide, $CH_2=CHBr$ (p. 65), vinyl ethyl ether, $CH_2=CH-O-C_2H_5$, and vinyl esters are known.

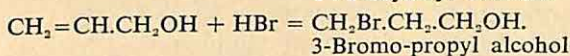
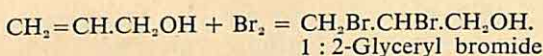
Allyl alcohol, $CH_2=CH-CH_2OH$, occurs in crude wood-spirit (about 0.2%); it may be prepared by heating glycerol in excess with oxalic (or better with formic) acid and a little ammonium chloride at about 260° . With excess of oxalic acid and at lower temperature, we get formic acid from oxalic acid (p. 145). Here glycerol forms allyl alcohol.



Commercially, allyl alcohol is made from allyl chloride (p. 115) by hydrolysis with boiling $NaOH$ solution under pressure. Allyl alcohol is a colourless, mobile liquid (b.p. 97°) with an irritating smell. All allyl compounds have pungent smell. The alcohol has a burning taste, and is miscible with water, ethanol and ether in all proportions. It combines the properties of a primary alcohol and an olefine; on oxidation under suitable conditions, allyl alcohol gives an aldehyde and then an acid:

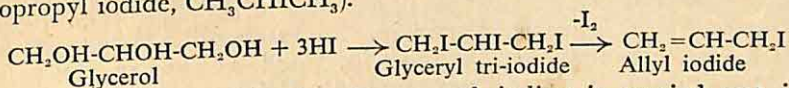


Sodium liberates hydrogen from the alcohol forming $CH_2=CH-CH_2ONa$; HCl gives allyl chloride, $CH_2=CH-CH_2Cl$. With Br_2 , HBr , etc. additive compounds are obtained.

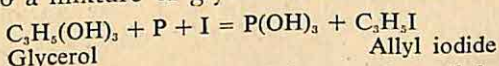


Allyl alcohol yields glycerol on oxidation with dilute KMnO_4 (cf., formation of glycol from ethylene, p. 59); with hydrogen in presence of platinum, it gives *n*-propyl alcohol. Allyl alcohol responds to the iodoform test (p. 93); it is an intermediate in the manufacture of synthetic glycerol (p. 115); a transparent resin is made from allyl phthalate.

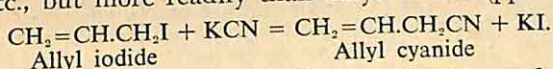
Allyl iodide, $\text{CH}_2=\text{CH}.\text{CH}_2\text{I}$, may be prepared by treating glycerol with hydriodic acid or yellow phosphorus and iodine. Glycerol and hydriodic acid probably give the tri-iodide which loses iodine to yield allyl iodide (but *excess* of HI reduces the latter to isopropyl iodide, $\text{CH}_3\text{CHICH}_3$).



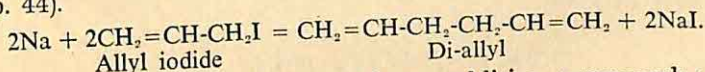
The reaction with phosphorus and iodine is carried out in an atmosphere of carbon dioxide, and the required amount of phosphorus added gradually to a mixture of glycerine and iodine.



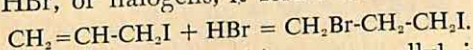
Allyl halides may also be obtained by reacting allyl alcohol with phosphorus halides or halogen acids as usual. Allyl iodide is a colourless liquid (b.p. 101°), with an odour of garlic. It is employed for introducing the allyl group into organic compounds. It reacts with KCN, K_2S , etc., but more readily than alkyl halides (pp. 73-75).



With sodium, diallyl is produced (cf., formation of ethane from CH_3I , p. 44).

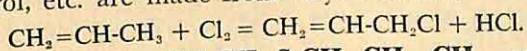


With HCl, HBr, or halogens, it forms additive compounds:

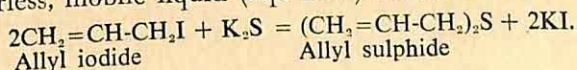


On distilling with potassium thiocyanate, allyl iodide gives allyl isothiocyanate or *oil of mustard* (p. 222).

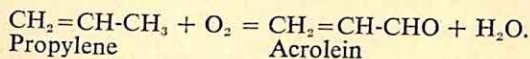
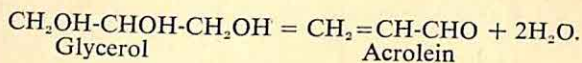
Allyl chloride, $\text{CH}_2=\text{CH}.\text{CH}_2\text{Cl}$, a liquid (b.p. 45°), is manufactured by chlorinating propylene at $500\text{--}600^\circ$ in 85% yield. Allyl alcohol, glycerol, etc. are made from allyl chloride.



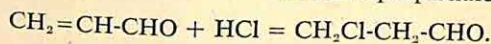
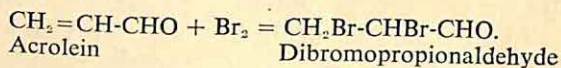
Allyl sulphide, $\text{CH}_2=\text{CH}.\text{CH}_2.\text{S}.\text{CH}_2.\text{CH}=\text{CH}_2$, occurs in onion and garlic (Latin *allium*, garlic) and is responsible for their odour. It is prepared by heating allyl iodide with alcoholic potassium sulphide. It is a colourless, mobile liquid (b.p. 140°) with a foul odour.



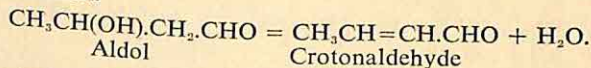
Unsaturated aldehydes.—The simplest is acryldehyde or *acrolein*, $\text{CH}_2=\text{CH}\cdot\text{CHO}$, prepared by distilling glycerol with potassium hydrogen sulphate (*vide* p. 115, test for glycerine), phosphorus pentoxide or anhydrous magnesium sulphate (dehydration). It is also formed when allyl alcohol is oxidised, or glycerine is passed over heated alumina (yield only 50%). A cheap commercial method is to oxidise directly propylene from petroleum cracking by air at $300\text{--}350^\circ$ in presence of cupric oxide.



Acrolein is a colourless, corrosive, toxic liquid (b.p. 52°) with a penetrating odour. It polymerises so readily (due to conjugated double bonds) that it can only be stored with a stabiliser (*e.g.*, 0.01% hydroquinone). Polymerised acrolein, an amber-like mass, is an insulator. Menthionine, an amino-acid, used as chicken feed for accelerated growth, is made from acrolein; U.S.A. made 1,035,000 lb. of it in 1954. The pungent odour from overheated fats and oils is due to acrolein (*acer*, sharp; *oleum*, oil). On reduction, it gives allyl alcohol, and on oxidation, acrylic acid. As an olefine, it adds on halogen or halogen acid (against Markownikoff's rule). LiAlH_4 reduces acrolein to allyl alcohol.

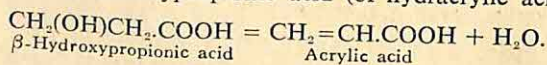


Crotonaldehyde, $\text{CH}_3\text{CH}=\text{CH}\cdot\text{CHO}$, occurs in *cis* and *trans* forms (p. 237) and is obtained by distilling aldol (p. 131) with dilute HCl. It is a colourless liquid (b.p. 105°), similar to acrolein in chemical properties. For its pungent odour and burning taste, it is used for denaturing alcohol in some countries. It is a solvent for resins, fats and waxes. U.S.A. makes *n*-butanol from crotonaldehyde by reduction.

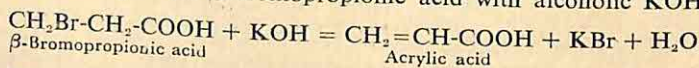


Unsaturated acids.—Acrylic acid, $\text{CH}_2=\text{CH}\cdot\text{COOH}$, the simplest, may be prepared:

- (i) By distilling β -hydroxypropionic acid (or hydracrylic acid):

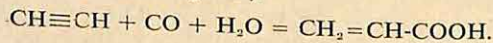


- (ii) By treating α - or β -bromopropionic acid with alcoholic KOH:

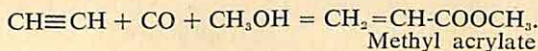


- (iii) By oxidising acrolein or allyl alcohol with silver oxide.

- (iv) By reacting acetylene, CO and water in presence of nickel carbonyl, $\text{Ni}(\text{CO})_4$, at atmospheric pressure (p. 69).



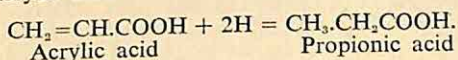
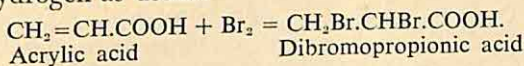
Methyl acrylate is obtained if methyl alcohol is used for water :



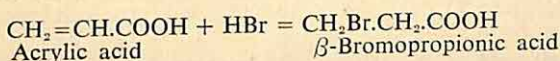
(v) Methyl lactate on acetylation and heating forms methyl acrylate :



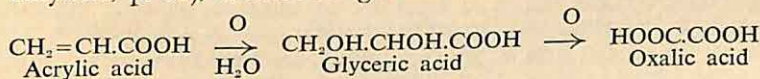
Acrylic acid is a colourless liquid (b.p. 140°), smelling like acetic acid and is miscible with water in all proportions. On standing, it polymerises to a solid. The adjacent double bond increases the tendency of the proton to escape; acrylic acid ($k_a = 5.5 \times 10^{-5}$) is stronger than propionic acid ($k_a = 1.4 \times 10^{-5}$). It adds up halogens and nascent hydrogen as usual:



With halogen acids, it forms a β -halogen propionic acid; the halogen attaches itself to the carbon farthest from the carboxyl (p. 181).

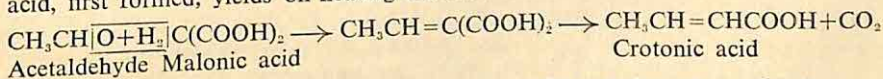


Dilute KMnO_4 oxidises it to dihydroxypropionic or glyceric acid (cf., ethylene, p. 59), and a stronger oxidant to oxalic acid:

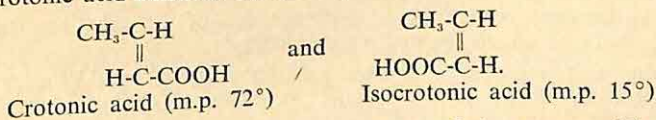


Acrylic resins, obtained from esters or amides of acrylic acid by polymerisation, are mainly used as denture bases, artificial eyes, lenses, etc. as they are transparent, water-white and resistant to age and light.

Crotonic acid, $\text{CH}_3\text{CH}=\text{CHCOOH}$, is formed by the oxidation of crotonaldehyde, by heating β -hydroxybutyric acid, or by the action of alcoholic KOH on α -bromobutyric acid. One interesting method is to heat acetaldehyde and malonic acid to 100° in glacial acetic acid solution. An unsaturated dibasic acid, first formed, yields on heating crotonic acid :

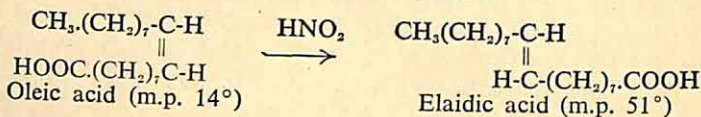


Crotonic acid exists in two forms, one is a solid and the other a liquid :



They differ only in the relative positions of the groups with respect to the double bond. It is a special case of geometrical isomerism (vide, maleic and fumaric acid, p. 250), better known as *cis-trans isomerism*. Glyceride of crotonic acid is the chief constituent of croton oil, whence the name. Both isomerides yield *n*-butyric acid on reduction, and oxalic acid, on oxidation, showing the similarity of their structure. Isocrotonic acid, the labile form, is partly transformed into crotonic acid on heating to 100° . Crotonic acid (*trans*) is weaker ($k = 2 \times 10^{-5}$) than isocrotonic acid (*cis*) having $k = 3.6 \times 10^{-5}$.

Oleic acid, $C_{18}H_{34}O_2$, occurs as a glyceride in fats and oils from which it is commonly prepared (p. 155). Olive oil is a rich source (76-86%). The acid is a pale yellow, practically odourless and tasteless liquid. On catalytic hydrogenation, it forms stearic acid, $C_{18}H_{36}O_2$, a solid (m.p. 69.4°). Oleic acid gets oxidised by air and becomes rancid. It is used for wool spinning. With a little nitrous acid which acts as a catalyst, oleic acid passes on to its more stable, *trans* isomer, *elaidic acid*, a solid. A little selenium at about 200° effects 66% conversion of oleic acid to elaidic acid.



Oleic acid, $C_{18}H_{34}O_2$, gives stearic acid, $C_{18}H_{36}O_2$, on reduction and dibromostearic acid, $C_{18}H_{34}Br_2O_2$, on bromination. Hence it has one double bond and like stearic acid, contains a straight carbon chain. HNO_3 oxidises oleic acid to pelargonic acid, $\text{CH}_3(\text{CH}_2)_7\text{COOH}$, and azelaic acid, $\text{HOOC}(\text{CH}_2)_7\text{COOH}$. The double bond lies, therefore, in the middle of the chain, i.e., at the 9:10 position; so oleic acid is $\text{CH}_3(\text{CH}_2)_7\text{CH=CH}(\text{CH}_2)_7\text{COOH}$. Ozonolysis lends additional support to this; the ozonide oleic acid forms with ozone splits, on hydrolysis, into pelargonic aldehyde, $\text{CH}_3(\text{CH}_2)_7\text{CHO}$, and azelaic acid monoaldehyde, $\text{OHC}(\text{CH}_2)_7\text{COOH}$. The structure has been confirmed by synthesis of oleic acid.

Ricinoleic acid, $C_{18}H_{33}(\text{OH})O_2$, 12-hydroxyoleic acid, is present in castor (*Ricinus communis*) oil as the glyceride. It represents 80-86% of the fatty acids of castor oil and is responsible for its purgative action which disappears on hydrogenation. Castor oil is a lubricant in airplane motors. Nitrous acid converts it to its solid, *trans* isomer, ricinelaidic acid (m.p. 53°).

Linolic or linoleic acid, $C_{18}H_{32}O_2$, a liquid, has two double bonds. It occurs as the glyceride in cottonseed and linseed oils—drying oils which form a hard, resinous product by absorbing oxygen from the air (p. 175). On hydrogenation, it gives stearic acid, $C_{18}H_{36}O_2$.

Linolenic acid, $C_{18}H_{30}O_2$, present in perilla seed and linseed oils, has three double bonds. These unsaturated acids appear to be essential food factors, their deficiency leads to dermatosis and eczema.

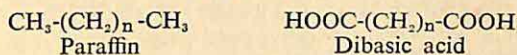
QUESTIONS

1. How could you prepare allyl alcohol? What is the action of HCl , HBr , metallic sodium, and oxidising agents on it? Give equations.
2. Starting from allyl iodide, how can you obtain (i) diallyl, (ii) allyl sulphide and (iii) oil of mustard?
3. How is acrolein prepared? Mention some of its reactions to show that it behaves both as an olefine and as an aldehyde.
4. Explain with reference to oleic acid how you would detect, and establish the position of the double bond in a chain of carbon atoms. B.Sc. Degree Exam., 1942. Annamalai Uni.
5. What is acrylic acid? Give a few methods for the formation of this compound. What compounds do you obtain by the action of (a) bromine, (b) HCl , (c) KMnO_4 on it? B.Sc., 1945, Nagpur Uni.

CHAPTER XXIII

THE SATURATED DIBASIC ACIDS

If two carboxyl groups occur in a molecule, it is a *dibasic acid*. The saturated dibasic acids are derived from the paraffins by replacing the two terminal methyl, $-\text{CH}_3$, groups by carboxyl, $-\text{COOH}$.



Saturated dibasic acids, $\text{C}_n\text{H}_{2n-2}\text{O}_4$.

Name	Formula	m.p. °C	$k_1 \times 10^5$	$k_2 \times 10^5$
Oxalic acid	$\text{HOOC}.\text{COOH}$	189.5	3800	11000
Malonic acid	$\text{HOOC}.\text{CH}_2.\text{COOH}$	134	177	4.37
Succinic acid	$\text{HOOC}(\text{CH}_2)_2.\text{COOH}$	183	6.6	4.50
Glutaric acid	$\text{HOOC}(\text{CH}_2)_3.\text{COOH}$	98	4.60	5.34
Adipic acid	$\text{HOOC}(\text{CH}_2)_4.\text{COOH}$	153	3.90	5.29
Pimelic acid	$\text{HOOC}(\text{CH}_2)_5.\text{COOH}$	105.5	3.33	4.87

The common names are for the lower members only. The higher acids are named after the corresponding paraffins, e.g., decanedicarboxylic acid is $\text{HOOC}(\text{CH}_2)_{10}.\text{COOH}$. The simplest dibasic acid is carbonic acid, $\text{HO}.\text{CO}.\text{OH}$, unknown in the free state. It does not, strictly speaking, belong to this series as it is *not* dicarboxylic. It is discussed in Chapter XXVI.

Oxalic acid, $\text{HOOC}.\text{COOH}$, the simplest dicarboxylic acid, occurs in plants of the *Oxalis* group; its acid potassium salt is found in sorrel, beet leaves and myrobalans (*Haritaki*). The insoluble, crystalline calcium oxalate occurs in cell walls; the bark of some eucalyptus trees contains about 20% of it. Derivatives of oxalic acid are also present in urine, specially under pathological conditions.

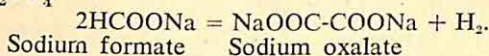
Preparation.—(1) In the laboratory, it is obtained by adding coarsely powdered cane-sugar (40 g.) to warm conc. HNO_3 (150 c.c.), contained in a litre-flask. A little vanadium pentoxide improves the yield. The reaction is carried out in a fume-chamber, as copious nitrous fumes are evolved. After the fumes have subsided, the liquid is concentrated in a dish on water-bath. On cooling, colourless crystals of oxalic acid appear. 1 part glucose gives 1.5 parts of oxalic acid. This is the method by which Scheele (1742-86) first obtained the acid in 1776. Like sugars, many other organic compounds such as glycol, alcohol, fats, cellulose, etc. yield oxalic acid on oxidation.

(2) Commercially, it was once made by oxidising cellulosic materials, e.g., sawdust from soft wood, which have the group, $-\text{CHOH}.\text{CHOH}-$. Gay-Lussac discovered the method in 1829.

The sawdust, made into a paste with about twice its weight of a strong solution of KOH and NaOH , is spread out in thin layers in iron pans and heated in air up to 250° . The fused alkali oxidises the cellulose to alkali oxalates. The mass is extracted with hot water. The aqueous extract is boiled with milk of lime, calcium oxalate filtered and washed with water. The alkaline filtrate is concentrated and used again. Requisite amount of dilute H_2SO_4 is

then added to the calcium oxalate. Calcium sulphate is filtered off and oxalic acid, $\text{HOOC.COOH.2H}_2\text{O}$, obtained by crystallisation.

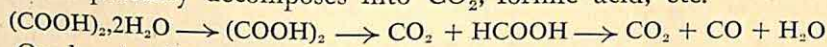
(3) Most of the commercial acid is made by a cheaper method. Carbon monoxide under pressure is passed into caustic soda; sodium formate, thus formed (p. 145), is *rapidly* heated to 390° , or to 300° with excess alkali; we get sodium oxalate. The free acid is obtained therefrom with H_2SO_4 .



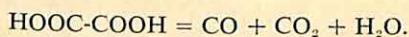
(4) Other methods of academic interest only are (i) oxidation of glycol (p. 110), (ii) hydrolysis of cyanogen (p. 213) and (iii) passing dry carbon dioxide under pressure at 360° over sodium or potassium:



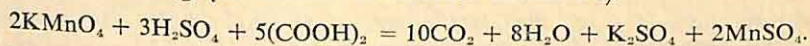
Properties.—Oxalic acid crystallises in large, colourless prisms with two molecules of water. The anhydrous acid is obtained by heating the crystals with carbon tetrachloride. It sublimes at about 200° and partially decomposes into CO_2 , formic acid, etc.



On heating in a sealed capillary tube, the anhydrous acid melts at 189.5° . The hydrated acid (m.p. 101°) is soluble in water, more freely in alcohol and only sparingly in ether. The anhydrous acid is much more soluble in dry ether. Oxalic acid and its soluble salts are poisonous. They remove calcium from the blood and tissues as insoluble calcium oxalate. *Halogeton*, a weed containing oxalic acid, kills cattle that graze on it. Conc. H_2SO_4 breaks up oxalic acid at about 100° into CO_2 and CO (*cf.*, formic acid, p. 147). *No charring takes place.*



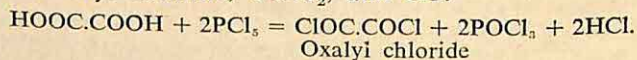
It is readily and *quantitatively* oxidised by KMnO_4 in acid solution to CO_2 on warming (difference from other members).



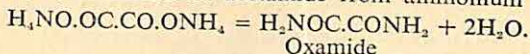
This is utilised for standardising permanganate solutions and estimating oxalates. Ferric salts oxidise the acid similarly; nascent hydrogen *e.g.*, from zinc and H_2SO_4 , reduces it to glycollic acid.



As a fairly strong acid, it turns litmus red, decomposes carbonates and reacts with some metallic oxides. The acid forms two types of salts, acid and neutral (*cf.*, salts of sulphuric and carbonic acid), *e.g.*, pot. hydrogen oxalate, HOOC.COOK , and pot. oxalate, KOOC.COOK ; it gives normal and acid esters with alcohols. With excess of PCl_5 , anhydrous oxalic acid produces the acid chloride, called oxalyl chloride, a colourless liquid (b.p. 64°) used in some organic syntheses. It readily splits into carbonyl chloride, COCl_2 , and CO .



Oxalic acid forms no anhydride. On dry distillation, ammonium oxalate yields the amide (cf., formation of acetamide from ammonium acetate, p. 165).



Oxamide gives cyanogen on heating with P_2O_5 (p. 213) and oxalic acid on hydrolysis. Oxalic acid also forms a half-amide, $\text{HOOC}.\text{CONH}_2$, called oxamic acid. Amic acids are half-amides and half-acids, derived from dicarboxylic acids.

Uses.—Oxalic acid is used as a mordant in dyeing and cloth printing and also in cleaning leather. Potassium ferrous oxalate, $\text{K}_2\text{Fe}(\text{C}_2\text{O}_4)_2 + \text{H}_2\text{O}$, is a photographic developer. Oxalic acid is employed in volumetric analysis. It is a constituent of most metal polishes. Potassium quadroxalate or 'salt of sorrel', $\text{KHC}_2\text{O}_4.\text{H}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O}$, removes ink-stains and iron-moulds from cloth, and bleaches straw (for hats). The acid dissolves rust from iron pipes of radiators in automobiles and is used in their cleaning.

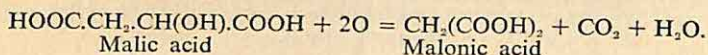
Tests.—(1) Oxalic acid or its salts decolorise KMnO_4 solution (acidified with dilute H_2SO_4) on warming.

(2) A neutral solution of an oxalate forms with calcium chloride a white ppt. insoluble in acetic acid. This is utilised in estimating calcium.

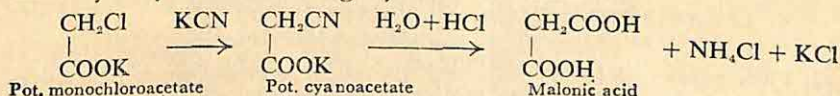
(3) The solid acid or its salts yield CO and CO_2 when warmed with conc. H_2SO_4 . The former burns with a blue flame.

In India oxalic acid is made from *Terminalia Arjuna* bark which contains calcium oxalate.

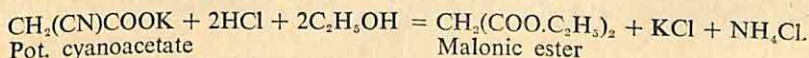
*** Malonic acid, $\text{HOOC}.\text{CH}_2.\text{COOH}$,** occurs as calcium salt in beet-root; it was first obtained in 1858 by oxidising malic acid with chromic acid, whence the name.



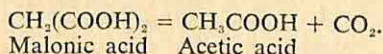
Malonic acid is commonly made by heating potassium monochloroacetate with aqueous pot. cyanide; the cyano-acetate formed, is then hydrolysed with strong hydrochloric acid.



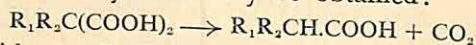
From the dried mass malonic acid is extracted with ether. Diethyl malonate which is far more important than the acid for its synthetic uses, is obtained similarly from dry potassium cyano-acetate, HCl gas and alcohol. Hydrolysis and esterification take place simultaneously. The ester may also be obtained by heating cyanoacetic acid (p. 186) with alcohol and sulphuric acid.



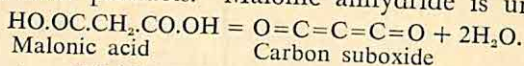
Malonic acid is a white, crystalline solid (m.p. 134°) easily soluble in water, alcohol and ether. Heated above its melting point, it loses carbon dioxide and forms acetic acid.



By this reaction, typical of acids having two -COOH groups attached to the same carbon, fatty acids may be obtained:

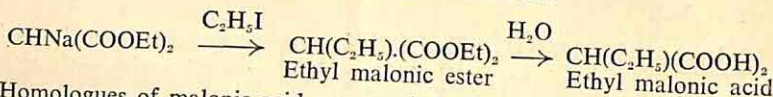
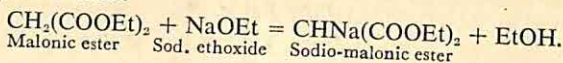


Malonic acid, on distillation with P_2O_5 , gives carbon suboxide, C_3O_2 , a poisonous gas (b.p. 7°) with intolerable smell. Carbon suboxide yields with water malonic acid, with HCl malonyl chloride, with ammonia malonamide, and with alcohol ethyl malonate. It readily polymerises to solid products. Malonic anhydride is unknown.

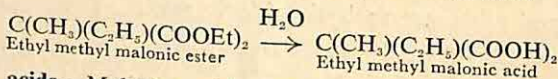
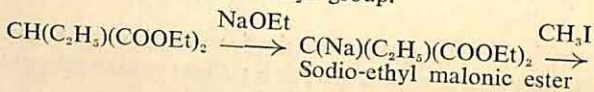


Malonic ester, $\text{CH}_2(\text{COOEt})_2$, is a colourless liquid (b.p. 198°) with a pleasant smell. Like aceto-acetic ester (p. 198), it contains the group $\text{-CO-CH}_2\text{-CO-}$, and is a tautomeric mixture of *keto* and *enol* forms. The hydrogen atoms of $\text{-CH}_2\text{-}$ group can be replaced by sodium one by one and CO_2 driven off from the free acid. Malonic ester is a valuable synthetic agent.

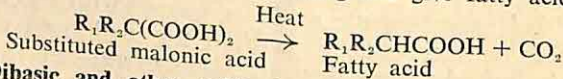
Synthetic uses: (i) Substituted malonic acids.—Malonic ester forms with sodium or sodium ethoxide in alcohol, a sodium derivative. The latter, in alcoholic solution, reacts with alkyl halides on boiling to produce different substituted malonic esters. On hydrolysis, these esters yield the corresponding substituted malonic acids.



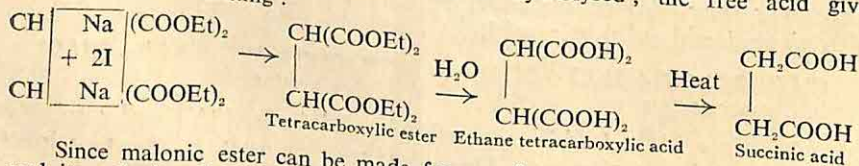
Homologues of malonic acid, e.g., methylmalonic acid, can thus be obtained. The second hydrogen atom of the methylene group may likewise be replaced by sodium and substituted by an alkyl group.



(ii) Fatty acids.—Malonic acid and its alkyl substitution products (as obtained above) part with CO_2 on heating and give fatty acids.

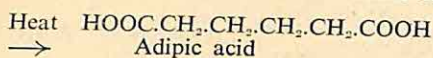
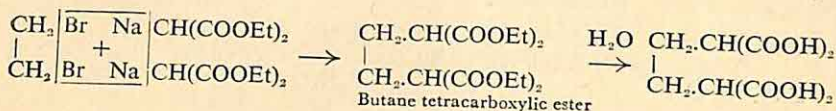


(iii) Dibasic and other polybasic acids.—(a) The sodium derivative, with iodine, yields tetracarboxylic ester. This is hydrolysed; the free acid gives succinic acid on heating:

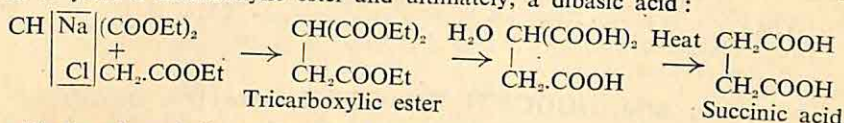


Since malonic ester can be made from a fatty acid (p. 241), succinic acid and its substituted products may be obtained from fatty acids.

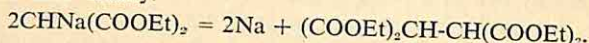
(b) Higher dibasic acids result on treating sodium malonic ester with alkylene halides having the two halogen atoms in the end positions.



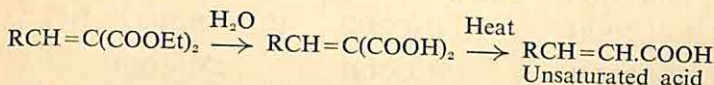
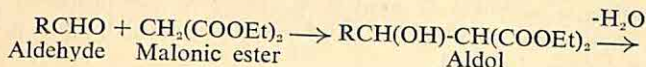
(c) Similarly, sodium malonic ester reacts with halogen-substituted fatty acids to yield a tricarboxylic ester and ultimately, a dibasic acid:



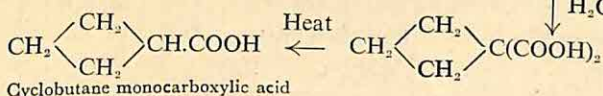
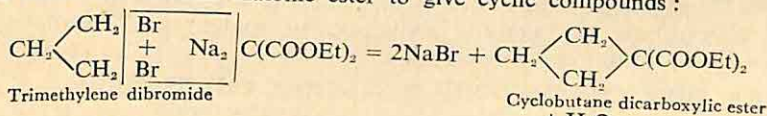
(d) On electrolysis, sodium malonic ester yields tetracarboxylic ester and hence, succinic acid finally.



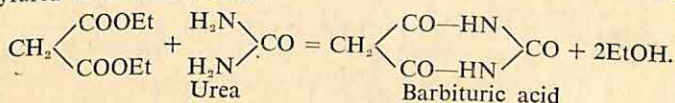
(iv) **Unsaturated acids.**—Malonic ester reacts with aldehydes to give unsaturated acids. An intermediate aldol formation explains the reaction.



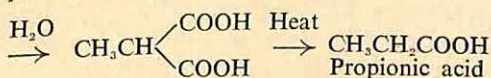
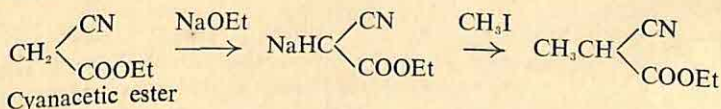
(v) **Cyclic compounds.**—Ethylene dibromide and similar dihalogen derivatives react with sodium malonic ester to give cyclic compounds:

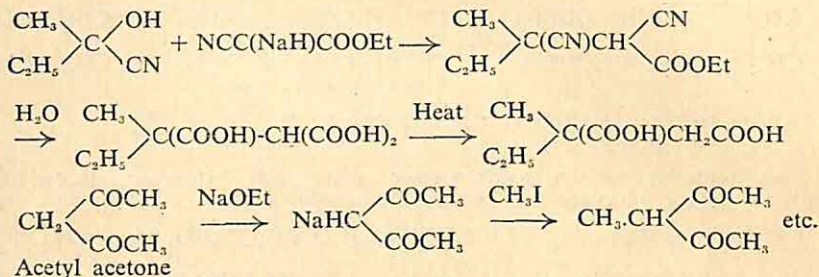


(vi) **Heterocyclic compounds.**—Malonic ester combines with urea forming malonylurea or barbituric acid:



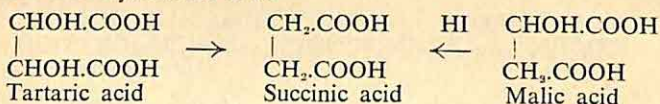
These reactions are not characteristic of malonic (and acetoacetic) ester alone. Whenever a $-\text{CH}_2-$ group occurs between two negative groups such as $-\text{CO}-$, $-\text{CN}$, etc., the hydrogen of the $-\text{CH}_2-$ group can be replaced by metals like Na, K, etc. Hence such syntheses are possible with other similar compounds, e.g., cyanacetic ester, $\text{CN} \cdot \text{CH}_2 \cdot \text{COOEt}$, or acetyl acetone, $\text{CH}_3\text{COCH}_2\text{COCH}_3$.



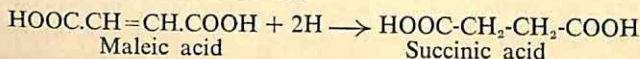


Succinic acid, $\text{HOOC-CH}_2\text{-CH}_2\text{-COOH}$, was first mentioned by Agricola in 1546 as a 'salt' obtained by the dry distillation of amber, a fossilised resin, found in the shores of the Baltic sea (Latin *succinum*, amber). It occurs in many plants (*e.g.*, lettuce), lignites, etc. About 1% succinic acid is formed during alcoholic fermentation (p. 89). Amber is distilled for colophony, and succinic acid is a bye-product.

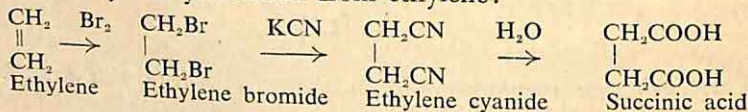
Preparation.—(i) Succinic acid is made by fermentation of tartrates or malates with yeast. It is a case of reduction which can as well be effected with hydriodic acid.



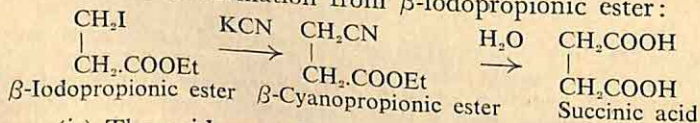
(ii) Unsaturated acids, maleic or fumaric, are reduced to succinic acid. Electrolytic or catalytic reduction of maleic acid (made from benzene) is a commercial method.



(iii) It may be synthesised from ethylene:



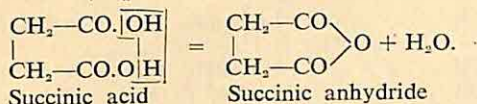
It is a *complete synthesis* as ethylene can be obtained from carbon and hydrogen. The constitution of the acid follows from this synthesis as also from its formation from β -iodopropionic ester:



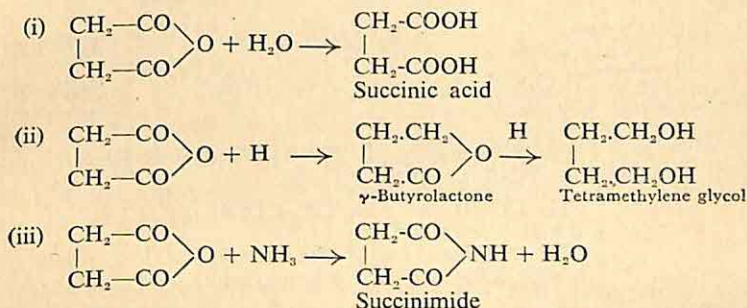
(iv) The acid may also be obtained from malonic ester and iodine (p. 242).

Properties.—Succinic acid is a colourless, crystalline solid (m.p. 185°), moderately soluble in water and ethyl alcohol, and almost insoluble in ether. With excess glycol, the acid forms linear polyesters on heating, these are known as *alkyd resins*. The acid is very weak; it forms acid chlorides, salts and esters as usual. A strong aqueous solution of pot. succinate, on electrolysis, gives ethylene (p. 57). When

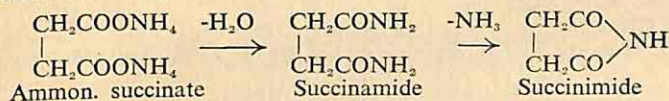
heated, it *readily* forms the anhydride (cf., action of heat on γ - and δ -hydroxy acids, p. 189); distillation of the acid with acetic anhydride or acetyl chloride gives a much better yield. Succinic anhydride is a crystalline solid (m.p. 120°), used in making some dyes.



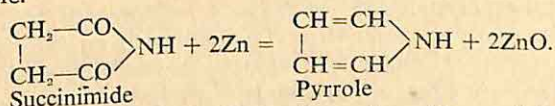
The anhydride yields (i) the original acid when boiled with water or dilute alkali; (ii) a glycol on reduction with sodium and alcohol and (iii) succinimide when heated in a current of ammonia:



Succinimide is also formed when ammonium succinate is *rapidly* distilled (cf., formation of acetamide, p. 165). The amide, first formed, decomposes to imide.



Succinimide, a white crystalline solid (m.p. 126°), is very weakly acidic and easily soluble in water. The hydrogen of the imido group, $-\text{NH}-$, lying between two electrophilic $-\text{CO}-$ groups, is replaceable by metals. The mercury salt is used in medicine; the potassium salt is decomposed by carbon dioxide. Distilled with zinc dust, succinimide forms pyrrole; sodium and alcohol reduce it to pyrrolidine or tetrahydropyrrole.

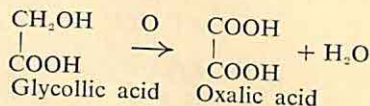
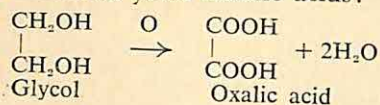


Isosuccinic acid, $\text{CH}_3\text{CH}(\text{COOH})_2$, isomeric with succinic acid, is really methylmalonic acid. It may be made from sodium malonic ester (p. 242). It is a crystalline solid (m.p. 130°). On heating, the acid loses CO_2 (instead of forming an anhydride) and yields propionic acid (cf., action of heat on malonic acid, p. 241).

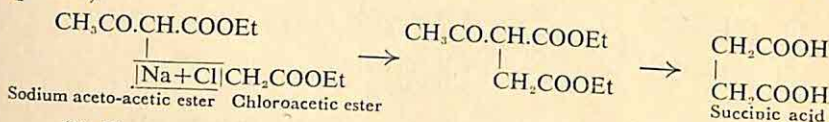
Adipic acid, a crystalline solid (m.p. 150°), is manufactured for making plastics and Nylon, a silk-substitute. Cyclohexanol (obtained by hydrogenating phenol, a coal-tar product) or cyclohexane, oxidised with nitric acid or air gives adipic acid. It was first obtained by oxidising fats (Latin *adeps* fat) with HNO_3 , hence the name. Long chain molecules of Nylon consist of condensation products of adipic acid and 1,6-diaminohexane, $\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$.

The molten mass of acid and diamine is passed at about 200° through a fine orifice and the fibre strengthened by cold-drawing.

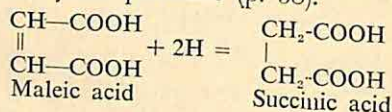
General methods of preparation.—(1) Glycols or hydroxy-acids, on oxidation, yield dibasic acids:



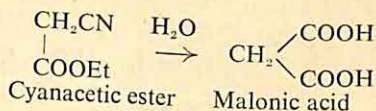
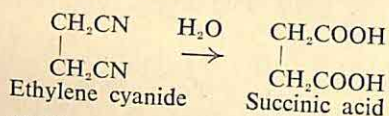
(2) Sodium aceto-acetic ester may be condensed with a chloro-fatty acid. The product, on *acid hydrolysis*, yields a dibasic acid. Homologues of malonic acid can thus be obtained from malonic ester (p. 242).



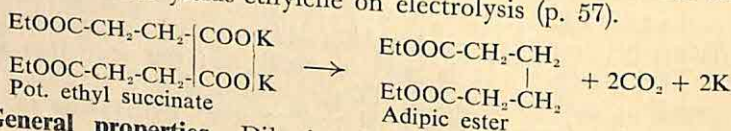
(3) Unsaturated dibasic acids, on reduction, give saturated dibasic acids just as ethylenes yield paraffins (p. 58).



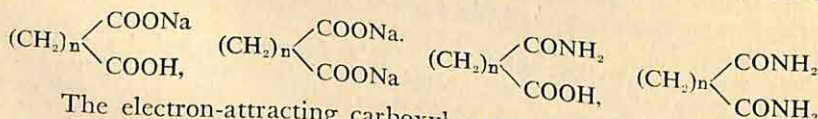
(4) Dicyanogen compounds or cyano-fatty acids, on hydrolysis, form dibasic acids:



(5) Potassium alkyl salts of lower dibasic acids, on electrolysis, produce higher dibasic acids as esters at the anode. Succinic acid or potassium succinate yields ethylene on electrolysis (p. 57).

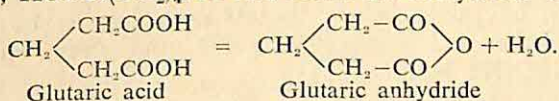


General properties.—Dibasic acids are colourless, crystalline solids. The lower members are quite soluble in water but the solubility decreases with increase in mol. wt. An acid with an odd number of carbon atoms is more soluble, and has a lower melting point than the one with an even number immediately preceding it in the series. These contrasts become less marked in acids with higher mol. wts. None is steam volatile. As dibasic acids, they form two series of derivatives:



The electron-attracting carboxyl group facilitates the escape of the proton from an adjoining carboxyl group; thus oxalic acid ($k_1 = 3.8 \times 10^{-2}$) is much stronger than acetic acid ($k = 1.86 \times 10^{-5}$) in its

first dissociation. The inductive effect, however, diminishes rapidly as the distance between the two -COOH groups increases. Thus oxalic acid is stronger than malonic acid which again is stronger than succinic acid. And the k_2 values are all less than the k_1 values due to the fact that the negatively charged -COO^- ion, after first dissociation, tends to suppress, by its repulsion of electrons, the ionisation of the other -COOH group (*vide* table on p. 239). Oxalic acid and acids with two carboxyl groups attached to the *same* carbon, lose CO_2 when heated, forming fatty acids (*cf.*, malonic acid, p. 241). Higher dibasic acids thus form internal anhydrides by losing a molecule of water. This is characteristic of acids having 4 or 5 C-atoms such as glutaric acid. Adipic acid, $\text{HOOC}(\text{CH}_2)_4\text{COOH}$, forms no anhydride on heating.



Inner imides are similarly formed when ammonium salts of dibasic acids are heated (p. 245). On vigorous oxidation, the higher members generally yield oxalic acid. PCl_5 gives di-acid chlorides.

QUESTIONS

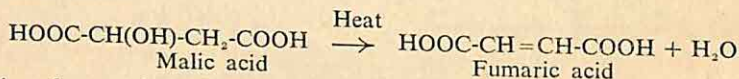
1. How would you prepare di-ethyl malonate in the pure state? Describe some of its synthetic uses. B.A., B.Sc., Bombay Uni., 1952; B.Sc. (Hons.), Dacca Uni., 1938; B.Sc., Muslim Uni. Aligarh, 1948.
2. Show by means of formulæ the structural relationship between succinic, malic and tartaric acids. How is succinic acid synthesised? B.Sc. Pass. Dacca Uni. 1933.
3. Outline a method for the commercial production of oxalic acid. Starting from oxalic acid how could you prepare (a) ethyl oxalate and (b) formic acid? Give equations. B.Sc. Pass. Calcutta Uni. 1940.
4. How does oxalic acid occur in nature? How is it prepared on a large scale? Deduce its constitutional formula. B.Sc. Pass. Calcutta Uni., 1932.
5. How could you prepare dibasic acids of the succinic acid series from fatty acids? Starting from malonic ester, how can the homologous acids of this series be obtained?
6. What is the action of alcohol, phosphorus pentachloride, strong and warm sulphuric acid, and acidified pot. permanganate solution on oxalic acid? Give equations.
7. Describe, with equations, how you can synthesise succinic acid from its elements. What is the action of heat on the acid?
8. How would you prepare diethyl malonate? Give an outline of the reaction by which different classes of compounds can be synthesised from this substance. B.Sc. Degree Exam. 1941, Madras Uni.
9. Give an account of the preparation of ethyl malonate and its uses as a synthetic reagent. B.Sc. Degree Exam., 1941, Travancore Uni.

CHAPTER XXIV

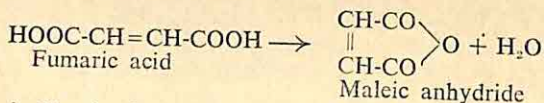
THE UNSATURATED DIBASIC ACIDS

The pair of isomeric acids—maleic and fumaric—are the simplest unsaturated dibasic acids. They have the common formula, $\text{HOOC}-\text{CH}=\text{CH}-\text{COOH}$, and are important from the stereo-chemical point of view. Maleic acid does not occur in nature, but free fumaric acid is found in some fungi, in the sap of the common medicinal herb *Fumaria officinalis* (whence the name) and in Iceland moss. Maleic acid is employed for making synthetic resins of glyptal type (p. 113) which, made into varnish, does not turn yellow. This acid inhibits rancidity of oils and milk powder. Ethene-1:1-dicarboxylic acid, $\text{CH}_2=\text{C}(\text{COOH})_2$, is unknown but its di-esters have been prepared; the acid possibly loses CO_2 and passes on to acrylic acid, $\text{CH}_2=\text{CHCOOH}$, readily.

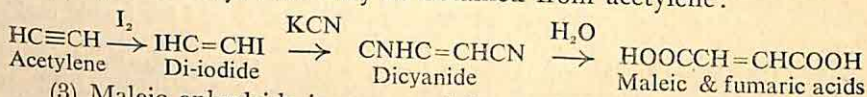
✓ **Preparation.**—(1) Heated slowly to about 145° , malic acid is mainly converted into fumaric acid (and, to a very small extent, to maleic acid) and water.



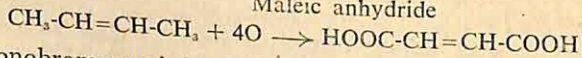
At about 185° , fumaric acid distils mostly as *maleic* anhydride which, on boiling with water, gives maleic acid.



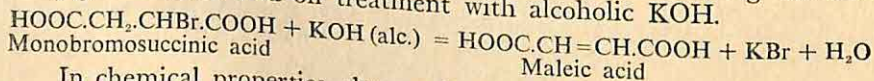
(2) Synthetically, both may be obtained from acetylene:



(3) Maleic anhydride is commercially made by the catalytic oxidation of benzene in vapour phase, or butyl-2-ene (from cracked 'petroleum') by air at 400° - 500° in presence of vanadium pentoxide. The yield is nearly 60%. The anhydride gives maleic acid with water.



(4) Monobromosuccinic acid (obtained by brominating succinic acid) gives maleic acid on treatment with alcoholic KOH.



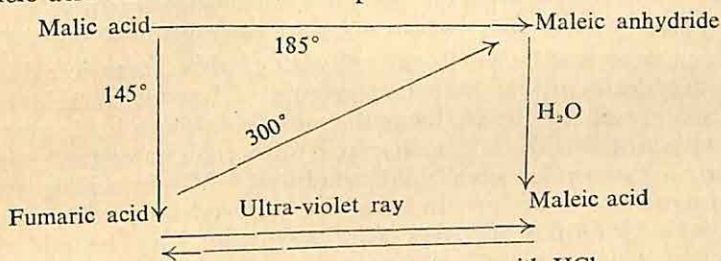
In chemical properties, due to the carboxyl groups and the double bond, they are alike; e.g., both

- (i) are reduced by sodium amalgam to succinic acid,
- (ii) decolorise bromine-water and give dibromosuccinic acid,
- (iii) take up water to form inactive malic acid,
- (iv) add on a molecule of HBr to yield bromosuccinic acid, and
- (v) produce two types of salts, esters, etc.

In other respects, they differ rather widely:

	Maleic acid	Fumaric acid
Melting point	130°	287° (in sealed tube)
Sp. gr.	1.590	1.635
Solubility in 100g. water at 25°	78.8 g.	0.7 g.
On heating	distils unchanged (with some maleic anhydride)	partly converted into maleic anhydride above 250°
(Primary) $K_a \times 10^2$	1.170	0.093
With baryta	precipitated	not precipitated
With $KMnO_4$ yields	meso-tartaric acid	racemic acid
Crystallises in	large prisms	small needles

Fumaric acid is more stable than maleic. The latter is more easily converted into the former—by exposure to light, on heating with HCl , I_2 or nitrous acid, etc. Fumaric acid partially passes on to maleic acid on distillation, or exposure to ultra-violet radiation.



Heat at 200° in a sealed tube or with HCl

✓ **Isomerism of maleic and fumaric acids.**—These acids have the same chain structure, functional groups and relative arrangement of atoms and groups. Both are optically inactive, having no asymmetric carbon. Their isomerism is thus different from that of lactic acid (p. 194) or tartaric acid (q.v.). van't Hoff (1874) assigned the following configurations to them.

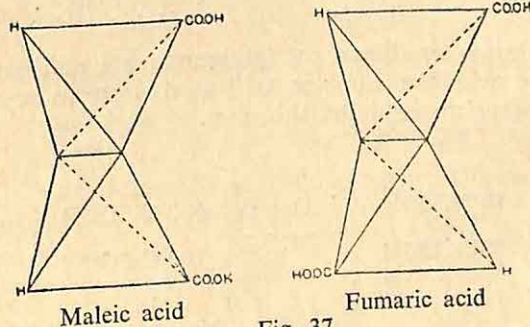
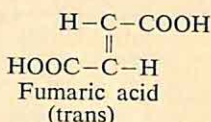
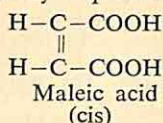


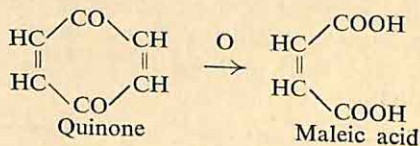
Fig. 37.

Or when ordinarily represented:

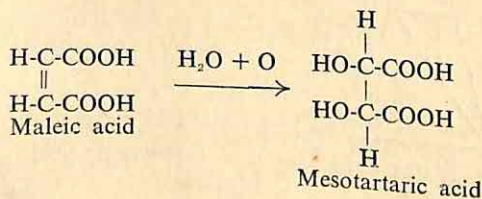


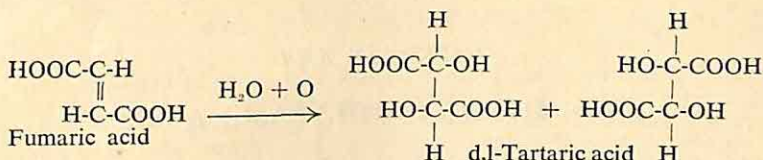
This is known as *cis-trans* or *geometrical isomerism* which is another kind of stereoisomerism. The one in which identical groups or atoms are closer *i.e.*, on the same side, is known as *cis-form* (Latin *cis*, on this side) while the other, in which they are remote, is called the *trans-form* (Latin *trans*, across). *Cis-trans* isomerism is possible in ethylenic compounds and co-planar cyclic systems, *e.g.*, inositols and benzene hexachlorides (q.v.). In saturated aliphatic compounds such isomerism is not met with; free rotation is possible around a single bond but not around a double bond. Thus we have only one dichloroethane, $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$, but two dichloroethylenes, $\text{CHCl}=\text{CHCl}$. X-ray analysis of dichloroethylene shows that in the *cis* isomer the distance between the chlorine atoms is 3.6 Å but in the *trans* compound 4.7 Å. The *cis-trans* isomers cannot be distinguished by any general method. As a rule, however, one in which the masses of the constituent atoms are most evenly distributed, has a higher m.p. and also greater stability. Optical and geometrical isomerism are the two forms of stereoisomerism.

Maleic acid readily yields an anhydride, while fumaric acid forms *maleic anhydride* only at high temperature. That maleic acid has the *cis* form is proved by the fact that the anhydride (both acids giving the same anhydride) yields only maleic acid with cold water (no rearrangement can occur under such mild condition). Maleic acid is stronger than fumaric due to the proximity of the carboxyl groups. Furthermore, considerable quantities of maleic acid are obtained by the oxidation of quinone in which carbonyl groups are in *cis*-position with respect to the double bond. (A little fumaric acid is simultaneously formed owing, in all probability, to the conversion of maleic acid into the more stable form).

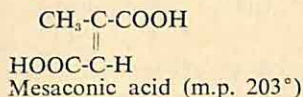
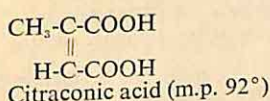


Sodium chlorate or dilute pot. permanganate oxidises maleic acid to meso-tartaric acid but fumaric acid to d,l-tartaric or racemic acid. Geometrical isomerism explains this fact.



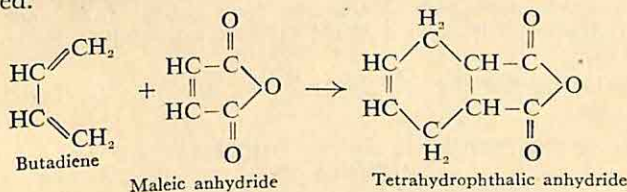


Similar cis-trans isomerism is exhibited by citraconic and mesaconic acids, obtained by rapid distillation of citric acid (q.v.). Citraconic acid (which is methylmaleic acid) forms the anhydride, but not mesaconic acid; the former is a stronger acid but less stable, than the latter. Citraconic acid is soluble in water and volatile in steam but mesaconic acid is sparingly soluble in water and non-volatile in steam. Mesaconic acid is formed when citraconic acid is heated with dilute nitric acid.



The isomerism of oleic and elaidic acids (p. 238) and of crotonic and isocrotonic acids (p. 237) is also of this kind. In fact, all ethylenic compounds of the type $\text{XHC}=\text{CHX}$ exhibit cis-trans isomerism. It may be noted here that the similarity in physical properties between geometrical isomerides is much less marked than between optical isomers (cf., lactic and paralactic acid, p. 195).

Maleic anhydride (m.p. 53°), 5-8% of which is obtained as a by-product in the oxidation of naphthalene to phthalic anhydride, is largely used in making alkyd resins. It is commercially made from benzene (p. 248). In benzene it reacts at room temperature with hydrocarbons having conjugated double bonds e.g., butadiene (*Diels-Alder Reaction*). The mixture is finally heated to 100° . 1,4-carbon atoms of the diene link with the ethylenic carbons of the anhydride with a shift of double bonds in the diene. Conjugated dienes are thus detected and estimated.



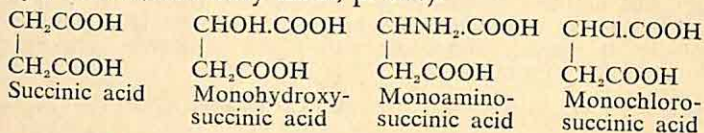
QUESTIONS

1. Discuss the isomerism of maleic and fumaric acids and explain why dibromo-ethane exists only in one form.
2. How is maleic acid obtained? How does it differ from fumaric acid? What is its use?
3. Starting from maleic acid, how can you obtain malic, succinic and tartaric acids?
4. Discuss the phenomenon of geometrical isomerism using maleic and fumaric acid as examples. How can they be converted into each other? B.A. Degree Exam. 1946, Madras Uni.
5. Discuss the stereo-chemistry of malic, fumaric and maleic acids. How can the latter two compounds be converted into one another? B.A. Degree Exam. 1941, Madras Uni.
6. Give an account of the special type of isomerism shown by unsaturated compounds and give two distinct examples. B.Sc. Degree Exam. 1942, Travancore Uni.

CHAPTER XXV

SOME HYDROXY-POLYBASIC ACIDS

One or more hydrogen atoms of methylene group, $-\text{CH}_2-$, in dibasic acids may be replaced by $-\text{OH}$, $-\text{NH}_2$, halogen, etc.; hydroxy-, amino-, etc. dibasic acids are thereby obtained (*cf.* formation of hydroxy-, amino-, etc. fatty acids, p. 180).

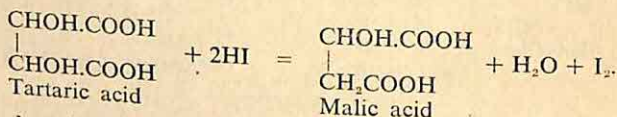


Substituted polybasic acids are similarly formed. Of these, the hydroxy-acids are the most important. The common hydroxy-dibasic acids are malic and tartaric acid.

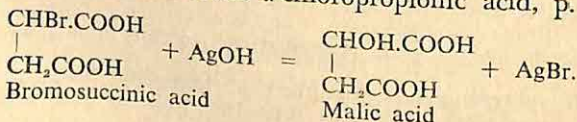
✓ **Malic acid, $\text{HOOC}\cdot\text{CH}_2\cdot\text{CHOH}\cdot\text{COOH}$,** occurs free and in abundance in many unripe fruits, *e.g.*, sour grapes, apples, mountain-ash berries, tomatoes, etc., and also in carrots, lettuce, etc. Tobacco and maples contain the acid calcium salt, and cherries the acid potassium salt. Scheele (1785) first isolated the acid from unripe apples (Latin *malum*) whence the name.

Preparation.—(1) Unripe mountain-ash berries are extracted with boiling water. The extract is treated with milk of lime. The neutral calcium malate, $\text{CaC}_4\text{H}_4\text{O}_5\cdot\text{H}_2\text{O}$, being insoluble, precipitates. It is filtered and dissolved in hot, dilute nitric acid, the acid calcium salt, $\text{Ca}(\text{C}_4\text{H}_3\text{O}_5)_2\cdot 6\text{H}_2\text{O}$, formed (which is soluble in water) crystallises out on cooling. It is decomposed with the calculated amount of dilute H_2SO_4 or oxalic acid. The filtered solution, on evaporation from water-bath, yields the free acid. Malic acid is obtained similarly from its calcium salt in sugar sand—a bye-product of the maple-sugar industry.

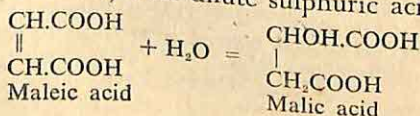
Synthetic methods: (i) By reducing tartaric acid with hydriodic acid:



(ii) By heating bromosuccinic acid with moist silver oxide (*cf.* formation of lactic acid from α -chloropropionic acid, p. 190).



(iii) It is manufactured in 100% yield by heating maleic acid (obtained from benzene) with dilute sulphuric acid under pressure.



The constitution of malic acid follows from these syntheses; it is hydroxy-succinic acid. Method (ii) may be regarded as a synthesis from elements inasmuch as bromosuccinic acid is made by the direct bromination of succinic acid which again can be obtained from carbon and hydrogen (p. 244). Malic acid of the market is no longer the l-acid from natural sources, but the synthetic inactive acid which is cheaper.

✓ **Stereoisomerism of malic acids.**—With an asymmetric carbon, malic acid should exist, like lactic acid, in three forms, d-, l-, and inactive malic acid. All these are known. The natural acid, e.g., from mountain-ash berries, is *lævo*-rotatory. The synthetic acid is inactive, being an equimolecular mixture (or loose compound) of dextro- and *lævo*-forms. The dextro-variety is obtained by the resolution of inactive acid. The cinchonine salts of d- and l-malic acids have different solubilities. The inactive acid is converted into the cinchonine salt; by fractional crystallisation, the d-acid is separated. It can also be obtained by treating dextro-tartaric acid with hydriodic acid. These optical isomers differ in some minor respects but chemically, they are the same. Thus, dl-malic acid has a higher m.p. (139°) than l-malic acid (m.p. 100°); the latter is more soluble in water than the former.

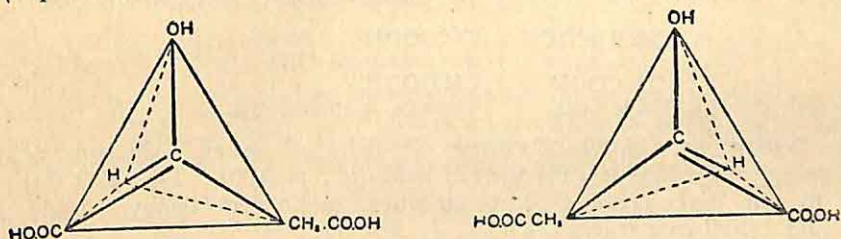
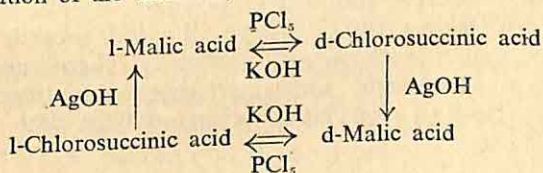


Fig. 38. d- and l-malic acids.

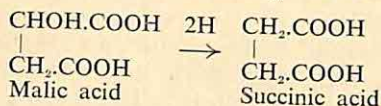
Some peculiarities have been observed regarding d- and l-malic acids. Thus l-malic acid with PCl_5 yields d-chlorosuccinic acid which, with moist silver oxide, gives d-malic acid. But d-chlorosuccinic acid with KOH gives l-malic acid. Again, d-malic acid gives, with PCl_5 , l-chlorosuccinic acid. l-Chlorosuccinic acid forms l-malic acid with moist silver oxide, but d-malic acid with KOH. In other words, reagents like PCl_5 , KOH, etc. reverse the optical rotation of the molecule, but not moist silver oxide.



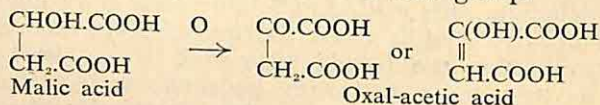
This phenomenon, discovered by P. Walden in 1893, is known as **Walden Inversion**. In some cases the inversion is quantitative, in others a mixture of d- and l-forms results. Some other optically active compounds, e.g., the amino-acids, behave likewise. When the concentration of the l-acid reaches 34%, the solution becomes inactive i.e. shows no rotation; but above this concentration, it is dextro-rotatory.

✗ **Properties.**—Malic acid is a colourless, crystalline and hygroscopic solid, readily soluble in water and alcohol but less soluble in ether. It forms a monoacetyl derivative with acetyl chloride, showing the pre-

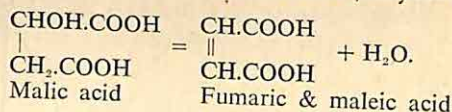
sence of a hydroxyl group. It is a fairly weak acid, $k_1 = 4.0 \times 10^{-4}$. On catalytic reduction with hydrogen, it gives succinic acid used for making synthetic resin. The process is commercially followed. Hydriodic acid effects the same change at 130° .



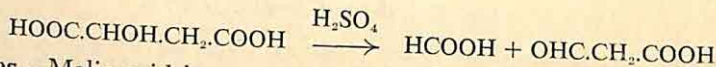
On careful oxidation, it gives oxal-acetic acid which exhibits keto-enol tautomerism like acetoacetic ester (p. 198). The secondary alcohol group, -CHOH- , is oxidised to a keto group.



When heated, malic acid loses water and forms fumaric acid at about 150° , and at 200° , mainly maleic acid but no anhydride (*cf.*, succinic acid, p. 245). Here it behaves as a β -hydroxy acid (p. 189).



With conc. H_2SO_4 , however, it behaves as an α -hydroxy-acid, forming an aldehyde and formic acid (*cf.*, p. 190). The -OH being α - to one carboxyl and β - to another, malic acid behaves both as α - and β -hydroxy acids.



Uses.—Malic acid is a purgative and also a remedy for throat sore. Sodium malate which tastes like common salt, replaces the latter when its use is undesirable. Malic acid is a substitute for citric acid in beverages, jellies, etc.

Tartaric acid, $\text{HOOC.CHOH.CHOH.COOH}$, occurs in four isomeric forms *viz.* (i) dextro- (d-), (ii) laevo- (l-), (iii) racemic (dl-) and (iv) meso-tartaric acid (Greek *mesos*, middle). These are classical examples of optical isomerism, and their thorough investigation by Pasteur led van't Hoff to correlate optical activity with molecular asymmetry.

Dextro-tartaric acid, $\text{C}_4\text{H}_6\text{O}_6$, is the ordinary acid found in various fruits such as prune, tamarind and grape, either free or as the acid potassium salt. During the later stages in the fermentation of grape juice to wine, the acid potassium tartrate, being insoluble in aqueous alcohol, separates as a brown crust, called *argol*, wine-lees, or tartar (p. 90). Scheele, in 1769, first isolated tartaric acid from argol wherefrom the commercial acid is still made. Of the sixteen acids—organic and inorganic—discovered by this Swedish apothecary, tartaric acid was the first.

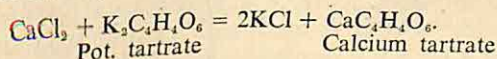
Properties of tartaric acids

Tartaric acid	d-	l-	meso-	racemic
m.p.	170°	170°	140°	206°
Sp. gr.	1.760	1.760	1.697	1.666
$[\alpha]_D$	+12	-12	0	0
Solubility at 20° g/100g. water	139	139	125	20.6
Crystal form	prisms	prisms	plates	rhombic
$K_1 \times 10^3$ at 25°	1.3	1.3	0.6	1.02
Mols. of water in Ca-salt	4	4	3	8

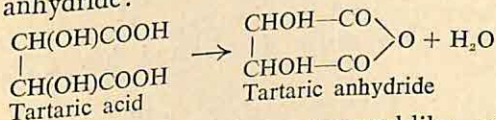
Crude tartar or argol (recrystallised argol is called cream of tartar) is dissolved in boiling water and nearly neutralised with chalk. Half of the original tartrate separates as the insoluble normal calcium salt, the other half remains in solution as neutral potassium tartrate.



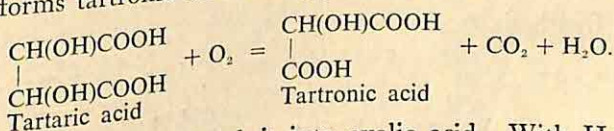
The calcium salt is filtered off and the filtrate treated with calcium chloride solution, calcium tartrate is again obtained. The calcium tartrate from both operations is decomposed by the calculated amount of H_2SO_4 and tartaric acid crystallised from the filtrate, after decolorisation with animal charcoal.



Properties.—d-Tartaric acid crystals are readily soluble in water, moderately soluble in alcohol and insoluble in ether. The aqueous solution is extremely sour to taste. On prolonged heating up to 150°, it forms the anhydride:



Above 170°, it chars emitting a caramel-like odour and forms pyruvic acid (p. 195), pyrotartaric or methylsuccinic acid, $\text{CH}_3\text{CH}(\text{COOH})\text{CH}_2\text{COOH}$, etc. On partial reduction, malic acid results but with hot hydriodic acid we get succinic acid. On mild oxidation, it forms tartronic acid like glycerol (p. 114).



Strong oxidising agents break it into oxalic acid. With H_2O_2 and a ferrous salt (Fenton's reagent), however, it gives dihydroxy-fumaric acid, $\text{HOOC.C(OH)=C(OH).COOH}$. As a dibasic acid, it forms acid and neutral salts, esters, etc. Normal alkali salts are soluble in water

but the acid salts of potassium and ammonium are insoluble. Tartaric acid reduces ammoniacal silver nitrate, hence its use in mirroring glass.

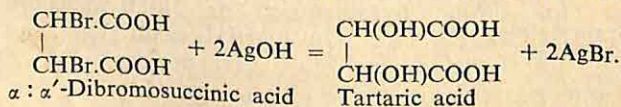
Lævo-tartaric acid is identical with dextro- in all respects except that (i) it shows an equal negative rotation, and (ii) its crystals have opposite hemihedral facets. It has been found in the leaves and fruits of a Sudanese tree (*Bauhinia reticulata*). The l-acid is usually made by resolving the racemic acid; equal quantities of the d- and l-varieties thus obtained are separated by suitable methods (p. 258).

Racemic or para-tartaric acid, $C_4H_6O_6 \cdot H_2O$, occurs in grape juice. In 1822 Kestner isolated it from the mother-liquor of cream of tartar. Berzelius (1830) showed that the acid had identical percentage composition with, but different properties from, the ordinary tartaric acid. He named it racemic acid (Latin *racemus*, bunch of grapes) and introduced the term *isomerism* to indicate their relationship. Racemic acid chemically resembles d- or l-acid but has different physical properties (p. 255). It crystallises with one mol. of water, and the acid or its calcium salt is much less soluble in water.

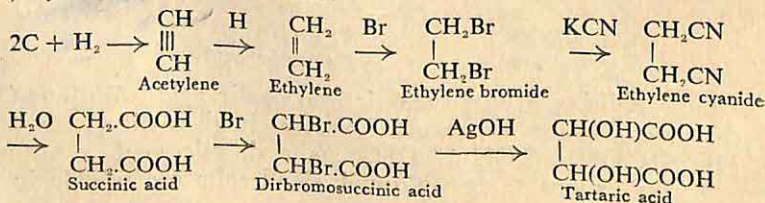
Synthetic tartaric acid is invariably inactive, being either racemic, or a mixture of racemic and meso-tartaric acid. Racemic acid is regarded as a loose compound of d- and l-acids; it is obtained when d- or l-tartaric acid is heated with water in a sealed tube at 175° , or boiled with a strong caustic soda solution. The process is called *racemisation*. When concentrated solutions of d- and l-acids are mixed, racemic acid separates with evolution of heat.

Meso-tartaric acid, $C_4H_6O_6 \cdot H_2O$, does not occur in nature. When ordinary tartaric acid is heated with caustic soda, meso-tartaric acid is formed together with racemic acid. It is also obtained by heating d-tartaric acid with water to about 175° , or with dilute acids. Unlike tartaric and racemic acid, its potassium salt is fairly soluble in water, but the calcium salt is more insoluble. On heating with water under pressure at about 170° , it is partially transformed into racemic acid. Chemically, mesotartaric acid is identical with other forms, but it cannot be resolved into active forms and has different physical properties (p. 255).

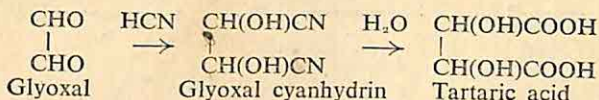
Synthesis.—(1) $\alpha:\alpha'$ -Dibromosuccinic acid, boiled with silver oxide suspended in water, yields d,l- and meso-tartaric acid:



(2) Synthesis from elements:



(3) Glyoxal gives dl- and meso-tartaric acid on treatment with hydrocyanic acid followed by hydrolysis:



Glyoxalic acid, reduced with zinc dust and acetic acid, gives racemic acid: $2\text{OHC.COOH} \rightarrow \text{HOOC.CHOH.CHOH.COOH}$. Fumaric acid, oxidised with dilute pot. permanganate, also yields racemic acid (p. 250).

Constitution.—Tartaric acid from analysis is $\text{C}_4\text{H}_6\text{O}_6$. It is dibasic, giving two types of salts and esters. So it has two carboxyl groups. The di-alkyl ester gives a di-acetyl derivatives. Hence, there are two alcoholic -OH groups. Tartaric acid may, therefore, be written as $\text{C}_2\text{H}_2(\text{OH})_2(\text{COOH})_2$. On reduction, it gives succinic acid having a straight carbon chain. Tartaric acid, therefore, should have the same. It splits off no CO_2 on heating, the two -COOH groups are not attached to the same carbon (cf. malonic acid, p. 241). It is quite stable so that the two alcoholic -OH groups are not linked to one carbon. Tartaric acid is a saturated compound. The structural formula consistent with these facts and confirmed by synthesis is: $\text{HO.OC.CH(OH).CH(OH).CO.OH}$.

Isomerism of the tartaric acids.—The acid has two asymmetric carbon atoms, each linked with the identical groups *viz.*, -OH, H, -COOH and -CH(OH)COOH. Four cases may arise regarding optical activity: (i) Both may turn the plane of polarisation in the clockwise direction, *i.e.*, towards the right. The result is dextro-rotatory acid (Model II in Fig. 39). The upper half of the molecule is not a mirror image of the lower half; if the former represents a (+) configuration, the latter is also positive.

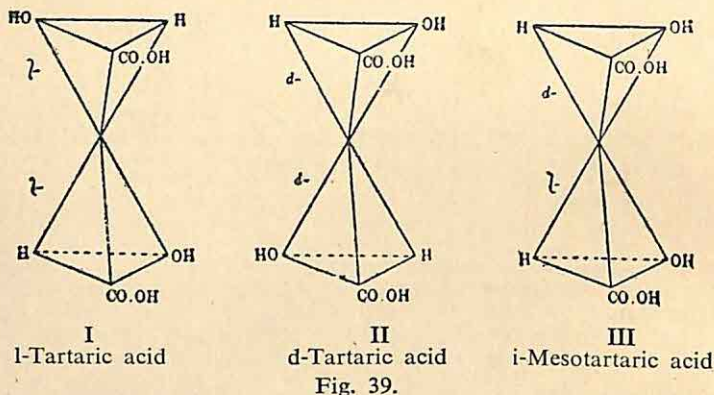
(ii) Both may rotate the plane of polarisation in the anti-clockwise direction, *i.e.*, towards the left. It is the laevo-rotatory acid (Model I in Fig. 39), and a mirror image of II; neither I nor II has a plane of symmetry.

(iii) The groups may be so arranged that one asymmetric carbon tends to turn the plane of polarisation to the right, while the other does to the left. One thus annuls the effect of the other. And since these two carbon atoms are linked to identical groups, their power of rotation, though opposite in direction, is equal in magnitude. Hence the molecule is optically inactive due to *internal compensation*, and incapable of being resolved. This is mesotartaric acid (Model III in Fig. 39). Unlike I and II, it has a plane of symmetry.

(iv) Lastly, a combination of *equal* amounts of d- and l-acids (Models I and II) is optically inactive obviously due to *external compensation*. This is racemic acid which can be resolved into the active forms by suitable methods.

Tartaric acid with two asymmetric carbon atoms should have 2^2 *i.e.*, 4 optical isomers. Let the mirror image of III be called IV. We then have the four possibilities. But the two asymmetric carbon atoms being identical, both

III and IV have a plane of symmetry; none is optically active. Hence the number is reduced to two only.



The term racemic has a wider meaning; it stands for optically inactive compounds consisting of equal amounts of dextro- and lævo-forms. Racemic compounds may be resolved into active forms by suitable methods. They are not mixtures, as when equal amounts of d- and l-forms are mixed together, heat is evolved. Moreover, the racemic compound does not resemble the d- and l-forms so closely. For example, racemic acid melts at 206° , while both d- and l-tartaric acid melt at 170° .

Tests.—(i) Tartaric acid or tartrates, when strongly heated, char rapidly giving an odour of burnt sugar.

(ii) Neutral tartrate solutions deposit, like aldehydes, a silver mirror from ammoniacal silver nitrate on warming.

(iii) Neutral solutions of tartrates form with calcium chloride solution a white ppt. of calcium tartrate in the cold, which is soluble in caustic soda or acetic acid (distinction from oxalic acid, p. 241).

(iv) With Fenton's reagent (hydrogen peroxide containing a trace of ferrous salt) and caustic soda, tartrates give a violet coloration.

Uses.—Tartaric acid is a constituent of saline drinks (*sherbet*) and cheap artificial wines. Sodium potassium tartrate, $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$, (*Rochelle salt*) is used in Fehling's solution, Seidlitz powder (a laxative) and in making mirrors. *Tartar emetic*, potassium antimonyl tartrate, $\text{C}_4\text{H}_4\text{O}_6\text{K}(\text{SbO})_2 \cdot \frac{1}{2}\text{H}_2\text{O}$, is an emetic in medicine and a mordant in dyeing and calico printing. Cream of tartar is employed in dyeing; baking powder contains cream of tartar and sodium bicarbonate; these with water at the baking temperature give CO_2 which raises the dough; it has limited solubility in the cold and so does not react with the bicarbonate.

Resolution of racemic compounds.—Synthetic products containing an asymmetric carbon are invariably racemic. They can be resolved into the d- and l-forms by three different methods—all discovered by Pasteur.

Mechanical method.—Pasteur separated simply by hand-picking under the microscope the crystals of sodium ammonium racemate, $\text{Na}(\text{NH}_4)\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$, into two groups, having opposite hemihedral (*i.e.*, exhibiting only *half* the full number) faces—one being the

mirror image of the other. These were found to be the two optical isomers, *d*- and *l*-. Crystals are *enantiomorphous* (*enantios*, opposite; *morphe*, form) if they are related as object and image like the left and the right hand.

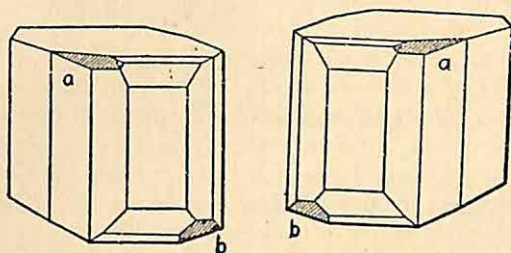


Fig. 40. Crystals of *d*- and *l*-sodium ammonium tartrate.

It fails if the two varieties do not crystallise separately and in sufficiently well-defined forms. For example, racemic acid itself cannot be thus resolved. Separation is possible only below the transition temperature, above which symmetric crystals are formed. In the above case, it is 28° . Luckily Pasteur (then a youngman of 26) worked below this temperature, though unknowingly.

Salt-formation method, by far the most useful, is based upon the fact that salts of the components of a racemic acid or base with an active base or acid generally have different solubilities. They can, therefore, be separated by fractional crystallisation. The original active components are then obtained by decomposing the salts. For example, to get *d*- and *l*-tartaric acids from the racemic acid, it is combined with *d*-cinchonine. The products, *d*-cinchonine *d*-tartrate and *d*-cinchonine *l*-tartrate, are not optical isomers. The latter, being less soluble, crystallises out first. Separation by fractional crystallisation is repeated until the rotation becomes constant. A racemic alcohol may be esterified with a *dibasic* acid to an *acid* ester which is combined with an optically active base, and resolved into its *d*- and *l*-components. These derivatives can also be separated by chromatographic methods, *e.g.*, *l*-menthyl *d*- and *l*-mandelates are adsorbed selectively on alumina; their separation is thus possible.

For resolution, optically active bases like quinine, strychnine, brucine, etc. and acids like tartaric acid, camphorsulphonic acid, etc., are commonly employed. Formation of molecular compounds (which crystallise as a whole) between the two salts obtained by combining the racemic base or acid with an active acid or base, may, however, make such separation impossible.

Biochemical method.—Some lower organisms *e.g.*, moulds and bacteria, selectively assimilate one optical isomer more rapidly than, and sometimes to the exclusion of, the other from a racemic compound. Thus, *Penicillium glaucum* (a species of green mould), if allowed to grow in ammonium racemate solution, eats up *d*-tartrate leaving aside the *l*-form, and *l*-lactic acid but not the *d*-form. Separation

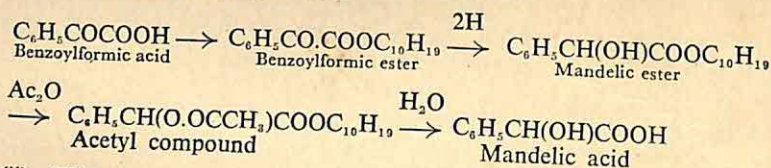
tion is slow and not always complete; one component is invariably lost. Simultaneously other products may be formed, rendering purification difficult.

An organism having a 'taste' for the d-form may be induced to assimilate the l-form, say, by making it starve and then supplying the l-form as food. It now gets accustomed to the l-form with a consequent dislike for the other.

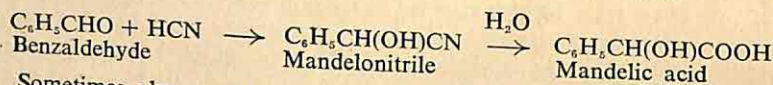
Racemisation.—d- or l-tartaric acid forms racemic acid on heating with water at 175° in a sealed tube (p. 256). This is apparently due to the conversion of half of the active compound into its isomeride by intramolecular change. Racemisation may be effected by (i) *the action of heat*: Lactic acid, amyl alcohol, tartaric acid, etc. are thus converted into inactive forms; and (ii) *chemical reagents*: l-Malic acid forms d-chlorosuccinic acid with phosphorus pentachloride (p. 253).

Asymmetric synthesis.—Synthetic methods give racemic compounds as d- and l-isomers are produced in equal amounts. By asymmetric synthesis is meant the production of optically active compounds from symmetrically constituted molecules *without resolution*. This has been achieved in three ways:

(i) **With optically active reagents**: An excess of the l-form of mandelic acid, $C_6H_5CH(OH)COOH$, has been obtained by esterifying benzoylformic acid with menthol (which is optically active), acetylating the reduced ester and finally hydrolysing the product formed. In such cases, one isomer hardly exceeds the other by more than a few per cent.



(ii) **With enzymes**: l-Mandelic acid, in large excess of the d-isomer, has been obtained by reacting benzaldehyde, C_6H_5CHO , with HCN in presence of the enzyme *emulsin* from almonds, and hydrolysing the product:



Sometimes almost cent per cent pure d- or l-variety can thus be obtained. This is not, however, essentially different from (i) inasmuch as enzymes are complex organic compounds which may be optically active. In vegetable and animal kingdoms, enzymes possibly play a similar role in producing optically active compounds in the pure state.

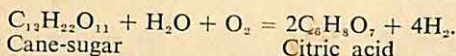
(iii) **With circularly polarised light**: Pasteur first suggested that natural circularly polarised light could produce optically active compounds. A faintly active [(α)_D not exceeding ± 0.5°] product has been obtained by the photochemical decomposition of α-bromopropionic ester, $CH_3CHBr.COOC_2H_5$, with dextro- and lævo-circularly polarised light (W. Kuhn). This may be regarded as an absolute asymmetric synthesis as neither an optically active agent nor any method of resolution is used. Here, the dextro-polarised light decomposes one, the lævo-polarised light the other component of the racemic mixture more quickly than the corresponding enantiomorph, so that the less attacked component predominates.

★ **Citric acid**, $HOOC.CH_2.C(OH)(COOH).CH_2.CO_2H$, occurs in pine-apple, bones and also in all citrus fruits (whence the name) e.g., lemon, lime, tomato, orange, etc., often with tartaric and malic acids.

Cow's milk contains a little (0.1%); as salts, it occurs in beet-root, potato, etc. Our blood serum contains about 25 mg. per litre, and we normally excrete about 0.5 g. daily with the urine. Citric acid is an intermediate product in the oxidative degradation of fats, proteins and carbohydrates in animal tissues. Scheele first isolated the acid from lemon-juice in 1784. With lime he obtained the calcium salt, which he decomposed with H_2SO_4 . Large quantities of citric acid are thus prepared even to-day in Sicily, California and other places where citrus fruits are abundant. Hawaii makes it from pine-apples. One ton of fresh lemon yields 15-50 lb. of citric acid.

Manufacture.—Extract of unripe lemons (containing 6.8% of the acid) is boiled to coagulate proteins. The decanted liquid is concentrated and treated with the requisite quantity of lime or chalk. The solution is boiled, calcium citrate being insoluble in boiling water, precipitates. It is decomposed with dilute sulphuric acid, insoluble CaSO_4 filtered off and the filtrate concentrated; we get transparent prisms of citric acid, $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$.

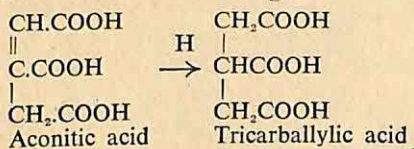
Citric acid is manufactured by fermenting purified molasses from sugar factories at pH 3.5 with certain moulds (*Citromyces*) at about 40° in open shallow pans of pure aluminium; the yield is above 50% of the sugar used; it takes 7-10 days. The acid is purified by forming the calcium salt as above. In England, Japan and U.S.A., practically all the citric acid is thus made with the common black mould *Aspergillus niger* which can withstand an acid reaction necessary to suppress most infections. The overall change is believed to be



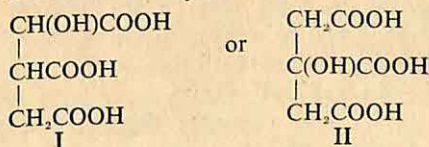
Tobacco waste which contains citric acid, may be a commercial source.

India imports citric acid (10,045 cwt. in 1955-56 valued at Rs. 14,19,520); it can be produced from molasses or citrus fruits in some states. U.S.A. makes about 30 million lb. annually.

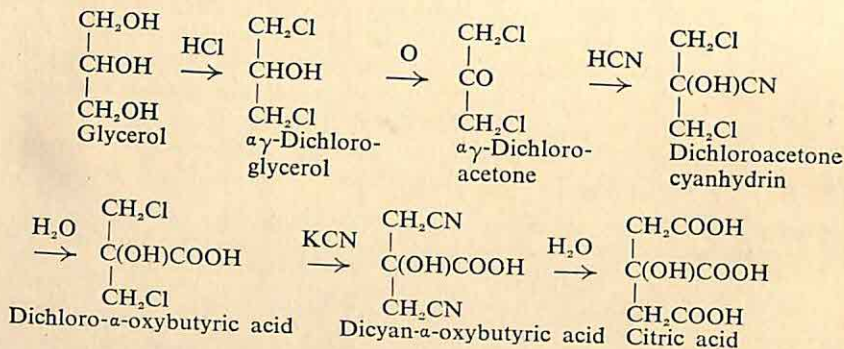
Constitution and synthesis.—(i) Anhydrous citric acid is $\text{C}_6\text{H}_8\text{O}_7$. (ii) It is tribasic as it forms three series of salts and esters; so it has three carboxyl groups. The tri-alkyl ester gives a mono-acetyl derivative; it has, therefore, one alcoholic -OH group. Citric acid may thus be written as $\text{C}_3\text{H}_4(\text{OH})(\text{COOH})_3$. (iii) The acid is saturated; on heating, it liberates no CO_2 ; hence two carboxyl groups are not linked to the same carbon. (iv) At 175° , citric acid loses a molecule of water, and partially forms aconitic acid, an unsaturated acid (cf., action of heat of β -hydroxy acids, p. 189). Aconitic acid yields tricarballic acid on reduction with sodium amalgam.



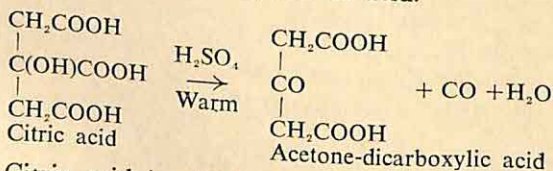
(v) Since citric acid is hydrated aconitic acid, it is



(vi) Its synthesis from glycerol decides in favour of II. The other, I, represents *iso*-citric acid, found in black-berry, which Fittig synthesised in 1889.



Properties.—Citric acid forms large rhombic prisms with one molecule of water of crystallisation, which it loses at about 130° . The hydrated acid melts at 100° on rapid heating, and between 135 – 152° if heated gently; but the anhydrous melts sharply at 153° . It is readily soluble in water and alcohol but insoluble in ether. The anhydrous acid crystallises from concentrated aqueous solution above 37° ; hydrated crystals are formed below this temperature. Citric acid is fairly strong, k_1 at 18° is 8.2×10^{-4} . Citrates do not reduce ammoniacal silver nitrate solution on warming, but on boiling, silver is slowly deposited. Citric acid may be distinguished from tartaric acid as calcium citrate, unlike calcium tartrate, is soluble in cold but *insoluble in boiling water*. It is also insoluble in acetic acid (*cf.*, tartaric acid, p. 258). This serves as a test for citrates. Citric acid or a citrate liberates CO on warming with strong H_2SO_4 , but *does not char* acid. The -OH being α - to one carboxyl and β - to another, it behaves both as α - and β -hydroxy acids. KMnO_4 also oxidises citric acid to acetone-dicarboxylic acid, but above 35° , oxalic acid results. Nitric acid breaks it up into oxalic and acetic acid.



Uses.—Citric acid is widely employed in making lemonades (it is palatable and easily digested), as a mordant in dyeing and calico printing. Ferric ammonium citrate and magnesium citrate (a laxative) are used in medicine. Sodium or potassium citrate relieves thirst in fever and prevents the clotting of blood in transfusion. Added to cow's milk, it also prevents clot formation in the infant's stomach. Mixed with pot. ferricyanide, ferric ammonium citrate is a coating for blue-print paper. Citric (like tartaric) acid prevents the precipitation of certain metallic hydroxides (*e.g.*, those of iron and copper) by alkalis, and is a

reagent in analytical chemistry. Tributyl citrate is a plasticiser for lacquers. It is used in making alkyd resins.

Tests.—(i) Warm citric acid or a citrate with conc. H_2SO_4 , carbon monoxide evolves; the mixture does not char but turns yellow.

(ii) Add calcium chloride solution to a neutral, concentrated solution of a citrate; no ppt. in the cold, a white ppt. of calcium citrate on boiling (insoluble in acetic acid).

(iii) To a neutral citrate solution, add sodium nitroprusside solution; a red colour is obtained, which becomes violet with acetic acid.

(iv) It gives no coloration with Fenton's reagent nor reduces ammoniacal solution of silver nitrate (cf., tartaric acid, p. 258).

Isocitric acid, $\text{HOOC} \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{COOH}) \cdot \text{CH}_2 \cdot \text{COOH}$, an optically active form of which occurs in black berries, readily forms a γ -lactone-dicarboxylic acid. It is not commercially important.

QUESTIONS

1. Discuss the constitution of citric acid. How is it manufactured? How would you convert propylene into citric acid? B.Sc. Subsidiary, 1952, Bombay Uni.

2. How many tartaric acids are known? How are they obtained? How do you account for their existence? B.Sc. Pass. 1932, Dacca Uni.

3. Discuss the constitution of tartaric acid. B.Sc. Pass, 1940, Calcutta Uni.

4. How is tartaric acid usually prepared? Deduce its constitutional formula. B.Sc. Pass, 1929, Calcutta Uni.

5. Explain van't Hoff and Le Bel's theory of molecular configuration and show how it accounts for the existence of the different varieties of tartaric acid. B.Sc. Pass 1934, Calcutta Uni.; B.Sc. Degree Exam. 1941, Annamalai Uni.

6. How are succinic, malic and tartaric acids related to one another? How can you convert one into another?

7. How do you arrive at the structure of citric acid? B.Sc., 1945 & 1947, Benares Hindu Uni.; B.Sc., 1948, Gauhati Uni., B.Sc., 1952, Calcutta Uni.

8. Explain, with illustrations (1) Walden inversion and (2) Resolution of racemic acid.

9. How can you synthesise malic and tartaric acids from their elements? How is mesotartaric acid obtained and in what ways does it differ from its isomers?

10. Give an account of the stereoisomerism of the tartaric acids. A.I.C. 1941; B.Sc. 1949, Gauhati Uni. B.Sc. 1952, Calcutta Uni. & Allahabad Uni.

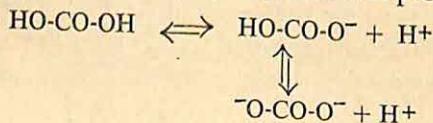
11. Explain and illustrate any four of the following terms; condensation, racemization, stereoisomerism, homology, and unsaturation. B.Sc. Pass, 1942, Patna Uni.

12. State briefly the methods of preparation of the various stereoisomers of tartaric acid. B.A. Degree Exam. 1942, Madras Uni.

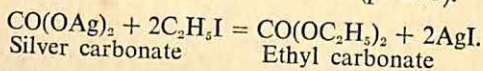
CHAPTER XXVI

THE DERIVATIVES OF CARBONIC ACID

Carbonic acid, H_2CO_3 .—An aqueous solution of carbon dioxide behaves as a dibasic acid; it contains only a little of carbonic acid in equilibrium with water and carbon dioxide. The acid is very weak (k for the first H is 3×10^{-7} at 18°), and has no free existence but its salts are quite stable. Its low strength appears to be largely due to its instability. Its anhydride, CO_2 , and metallic salts are described in text-books of inorganic chemistry. Carbonic acid, $\text{O}=\text{C} \begin{matrix} \text{OH} \\ \text{OH} \end{matrix}$ is the simplest of the organic dibasic acids; it is hydroxyformic acid. Two -OH groups attached to the *same* carbon make it unstable. The -CO-group being common to the -OH groups, it behaves as a dibasic acid, though two independent carboxyl groups are not present. It ionises as

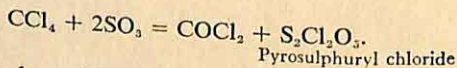
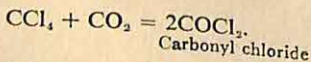


Esters of carbonic acid, $\text{CO}(\text{OR})_2$, are conveniently obtained by boiling silver carbonate with alkyl iodides. These may also be prepared by reacting alcohols with carbonyl chloride (p. 265).

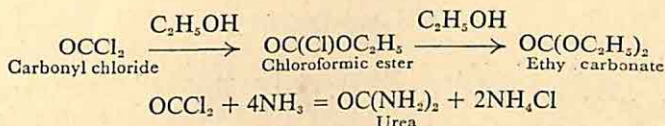


Alkyl carbonates are colourless, pleasant-smelling liquids which dissolve in water with gradual decomposition into alcohol and carbonic acid. Ethyl carbonate, a liquid, boils at 126° .

Carbonyl chloride, COCl_2 , is the acid chloride of carbonic acid; it is formed when chloroform decomposes in light and air (p. 78). J. Davy (1812) obtained it from carbon monoxide and chlorine in presence of sunlight and named it phosgene (*phos* light, *genes* born). Commercially, it is made by passing the gases over active charcoal at 200° or by passing carbon tetrachloride vapour and carbon dioxide over heated pumice stone. In the laboratory, it is prepared by the action of sulphur trioxide (contained in 80% oleum) on boiling carbon tetrachloride.

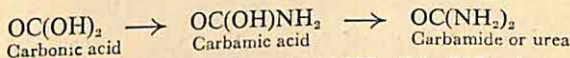


Carbonyl chloride is a colourless, highly poisonous gas (b.p. 8°) with a suffocating odour. It is readily soluble in benzene. The gas fumes in moist air, being hydrolysed into CO_2 and HCl . With alcohol, it forms ethyl carbonate, a solvent, and with NH_3 , the diamide or urea. Carbonyl chloride is used in making some dyestuffs. During the 1914-18 war, Germany introduced it as a poison gas.

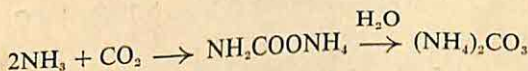


Like carbonic acid, ortho-carbonic acid, C(OH)_2 , has no free existence but its esters are known; ethyl ortho-carbonate, $\text{C(OC}_2\text{H}_5)_2$, is a liquid (b.p. 158°) with a pleasant odour.

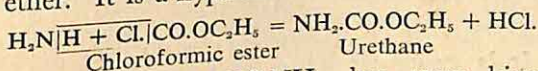
Amides of carbonic acid.—As a dibasic acid, carbonic acid forms two amides:



Carbamic acid, amino-formic acid, $\text{NH}_2\text{-CO-OH}$, does not occur free but its salts, esters and amides are known. Carbamide or urea is the most important derivative. Ammonium carbamate, $\text{NH}_2\text{COONH}_4$, is present in commercial ammonium carbonate, being formed by the interaction of ammonia and carbon dioxide. It may be extracted therefrom with alcohol. It is easily prepared by passing dry carbon dioxide into alcoholic ammonia. Ammonium carbamate is a white, crystalline powder. On warming with water, it yields ammonium carbonate:

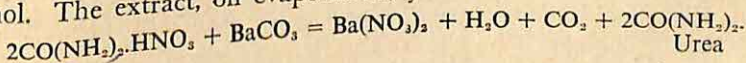


Urethanes.—Esters of carbamic acid, termed urethanes, are prepared by the action of ammonia on chloroformic ester. Urethane or ethyl carbamate is a crystalline solid (m.p. 50°), soluble in water, alcohol, and ether. It is a hypnotic.



Urea or carbamide, $\text{H}_2\text{N} \cdot \text{CO} \cdot \text{NH}_2$, has some historical importance, being the first organic compound synthesised in the laboratory in 1828 by Wöhler. It was isolated by Rouelle (1773) from urine (whence the name), where it occurs as the final decomposition product of proteins. The urine of mammals, fishes and some birds and reptiles contains urea; an adult normally excretes about 30 g. (nearly 2% of the urine) per day. Urea has been found in moulds; uric acid, present in our system, is a derivative of urea.

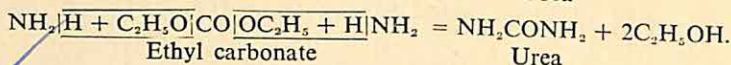
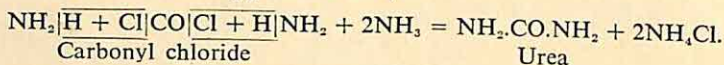
Preparation: (1) *From urine.*—On adding HNO_3 to a highly concentrated urine, the crystals of sparingly soluble urea nitrate, $\text{CO(NH}_2)_2 \cdot \text{HNO}_3$, separate. Urea is liberated from the nitrate with barium carbonate. From the dried mass, urea is extracted with alcohol. The extract, on evaporation, yields urea.



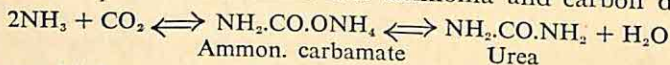
(2) *Wöhler's method.*—An aqueous solution of ammonium cyanate (a mixture of KCNO and $(\text{NH}_4)_2\text{SO}_4$) on evaporation to dryness on water-bath, gives urea and K_2SO_4 . Urea may be extracted therefrom with hot absolute alcohol in which K_2SO_4 is insoluble. By intramolecular change, ammonium cyanate forms isomeric urea. The reaction is reversible, equilibrium is reached at 93% conversion.



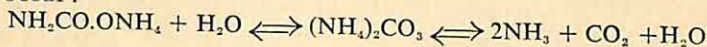
(3) *From acid chloride.*—Urea may be prepared from carbonyl chloride or ester of carbonic acid by reacting with ammonia (cf., formation of acetamide, pp. 162, 171).



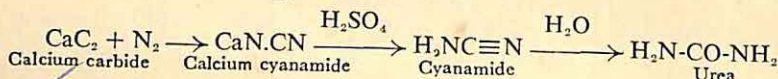
(4) Urea is manufactured by passing dry ammonia in large excess and carbon dioxide into an autoclave maintained at 130°-140° and 35 atmospheres. Ammonium carbamate, first formed, changes to urea and water. The conversion is about 40%. If ammonium carbamate is heated in the open, it dissociates into ammonia and carbon dioxide.



Due to high concentration of ammonia, the following side-reaction cannot occur:

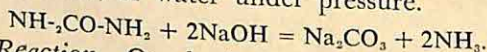


(5) Urea is also made by partial hydrolysis in feebly acid solution of cyanamide prepared from CaC_2 and nitrogen in the electric furnace (p. 220). This is no longer economical.

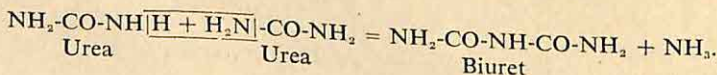


Properties.—Urea is a colourless, odourless, crystalline solid (m. p. 132°). It is readily soluble in water, moderately soluble in methanol, less so in ethanol, but insoluble in ether. The aqueous solution is neutral to litmus. It is a very weak monoacidic base ($k = 1.5 \times 10^{-14}$), forming salt with only *one* molecule of a monobasic acid. The nitrate, $\text{CO}(\text{NH}_2)_2 \cdot \text{HNO}_3$, and the oxalate, $[\text{CO}(\text{NH}_2)_2]_2 \cdot \text{H}_2\text{C}_2\text{O}_4$, are the important salts, both sparingly soluble in water and crystalline; they are utilised for the separation and detection of urea. Urea is hygroscopic, it rapidly absorbs moisture from the humid atmosphere.

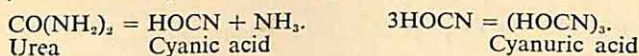
Reactions.—(i) Like other amides, urea is hydrolysed to ammonia by boiling alkalis, acids, or water under pressure.



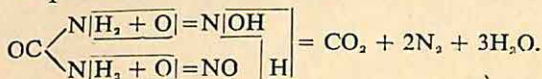
(ii) *Biuret Reaction.*—On slowly heating, urea melts and suddenly solidifies (at 150°-160°), forming biuret and ammonia. Biuret is a colourless, crystalline solid (m. p. 193°). Its aqueous solution develops a violet colour with NaOH and 1-2 drops of a *very dilute* CuSO_4 solution. It is a test for urea. But other compounds with two or more $-\text{CO} \cdot \text{NH}_2$ or $-\text{NH} \cdot \text{CO}-$ groups (e.g., oxamide, $\text{NH}_2\text{OC} \cdot \text{CONH}_2$, proteins, etc.) give this test.



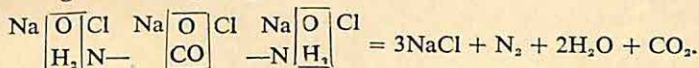
(iii) Heated rapidly above its m.p., urea forms cyanic acid which readily polymerises to cyanuric acid (p. 220).



(iv) Nitrous acid readily splits up urea into carbon dioxide, nitrogen and water (cf., the action of HNO_2 on primary amines, p. 204). Urea is, therefore, employed to remove nitrous acid from a reaction mixture where its presence is undesirable.

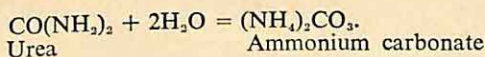


(v) Alkaline hypochlorite or hypobromite decomposes urea to water, nitrogen and carbon dioxide; the alkali retains the carbon dioxide and only nitrogen is evolved. Urea in urine is thus roughly estimated by measuring the nitrogen (p. 268).



(vi) When a neutral solution of mercuric nitrate is added to a solution of urea, a white, curdy ppt. of a basic compound, $2\text{CO}(\text{NH}_2)_2 \cdot \text{Hg}(\text{NO}_3)_2 \cdot 3\text{HgO}$, is obtained. In liquid ammonia, urea and alkali metals form salts such as $\text{NH}_2\text{CO.NHNa}$ and $\text{CO}(\text{NHNa})_2$.

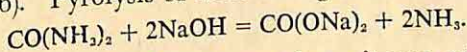
(vii) An enzyme, *urease*, found in soya-bean (*Glycine hispida*), hydrolyses urea to ammonium carbonate rapidly and quantitatively. This is utilised in estimating urea (p. 269). Soil bacteria similarly decompose urea of urine into ammonia and carbon dioxide.



(viii) Urea forms ring compounds; malonic ester and urea give malonyl urea or barbituric acid (p. 243).

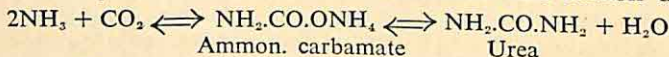
Diethyl barbituric acid, $\text{CO}(\text{NH-CO})_2\text{C}(\text{C}_2\text{H}_5)_2$, is the well-known hypnotic, veronal (or barbitone) so called because Emil Fischer, its discoverer, happened to wake up and look out of his carriage window at Verona after a visit to Baeyer to discuss its properties.

Constitution.—The molecular formula of urea is CON_2H_4 . Its formation from the acid chloride of carbonic acid, COCl_2 , or ethyl carbonate and ammonia (pp. 265-6), suggests that it is an amide (cf., formation of acetamide from acetyl chloride, p. 162 and ethyl acetate, p. 171). In neither case, the yield of urea is quantitative, and unlike diamides it forms stable salts with strong acids. The formation of ammonia, on hydrolysis, supports the diamide structure (cf., hydrolysis of amides, p. 166). Pyrolysis of urea also gives ammonia but no water.

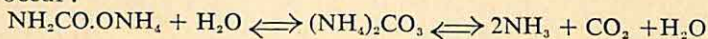


Liberation of nitrogen from urea by nitrous acid indicates the existence of two -NH_2 groups in the molecule (cf., action of HNO_2 on primary amines, p. 204). But it does not follow from the diamide formula why urea is monoacidic. An alternative structure, suggested

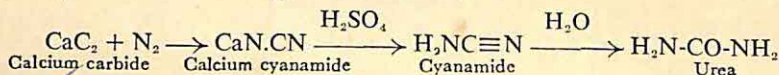
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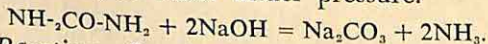


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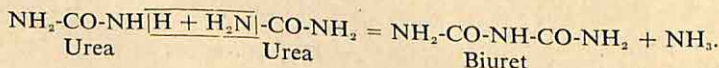


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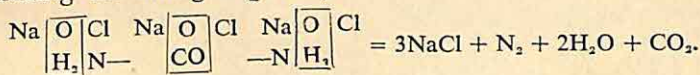
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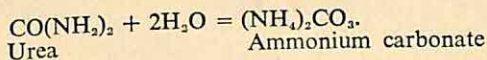


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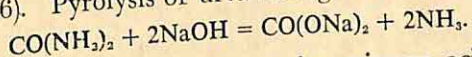
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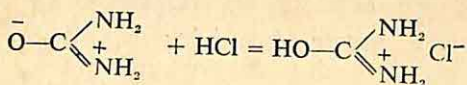
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by Werner, $\text{HN}=\text{C} \begin{smallmatrix} \text{O} \\ | \\ \text{NH}_2 \end{smallmatrix}$ explains the ease with which urea loses ammonia and forms cyanic acid on heating; but N is here quinquevalent. Chattaway's constitution, $\text{HO}-\text{C} \begin{smallmatrix} \text{NH} \\ // \\ \text{NH}_2 \end{smallmatrix}$ accounts for its monoacid nature and also why it gives O-alkyl derivatives but does not follow from its mode of formation. It cannot explain why urea gives no water on pyrolysis—even P_2O_5 splits off NH_3 from urea.

Urea is now believed to be a resonance hybrid of $\bar{\text{O}}-\text{C} \begin{smallmatrix} \text{NH}_2 \\ // \\ \text{NH}_2^+ \end{smallmatrix}$ and $\bar{\text{O}}-\text{C} \begin{smallmatrix} \text{NH}_2^+ \\ // \\ \text{NH}_2 \end{smallmatrix}$, and probably also of the diamide structure, $\text{O}=\text{C} \begin{smallmatrix} \text{NH}_2 \\ // \\ \text{NH}_2 \end{smallmatrix}$ which is consistent with the fact that from X-ray analysis the nitrogen atoms in crystalline urea are found to be identical, and the carbon-nitrogen bond length equal to 1.33Å which is intermediate between 1.48Å for C-N (e.g., in amines) and 1.28Å for C=N. Dipole moment value supports this hybrid structure. This zwitter-ion structure explains its monoacidic nature also; the proton from a strong acid being added to the negatively polarised oxygen atom:



Two nitrogen atoms linked to one carbonyl group make urea somewhat more basic ($k_b = 1.5 \times 10^{-14}$) than a monoamide, e.g. acetamide ($k_b = 3.1 \times 10^{-15}$).

Urea forms N-alkyl derivatives, e.g., $\text{O}=\text{C} \begin{smallmatrix} \text{NH}_2 \\ // \\ \text{NR}_2 \end{smallmatrix}$ as well as O-methylurea,

$\text{CH}_3-\text{O}-\text{C} \begin{smallmatrix} \text{NH}_2 \\ // \\ \text{NH} \end{smallmatrix}$ under suitable conditions. This is explained by assuming that urea behaves as a tautomeric compound (the tautomerides have not, however, been isolated):



Tests.—(i) Urea is detected by the biuret reaction (p. 266).

(ii) Add conc. HNO_3 , or a strong solution of oxalic acid to an aqueous solution of urea, a white crystalline ppt. of urea nitrate or oxalate is obtained.

(iii) Add sodium hypobromite solution (NaOH added to bromine-water) to an aqueous solution of urea, nitrogen is evolved.

(iv) Add sodium nitrate solution and then dilute HCl to urea solution, carbon dioxide and nitrogen are evolved.

Uses.—For making plastics with formaldehyde, huge quantities of urea are used. Urea-formaldehyde resin is used in making plywood. The resin is a factor in the anticrease process for cotton. It is an excellent fertiliser, having 47% available nitrogen. But plants cannot assimilate urea directly as they do nitrates; soil

bacteria split it up into CO_2 and NH_3 which soil and root bacteria convert into nitrates. For making veronal, a soporific, urea stibamine, $(\text{HO})_2\text{SbO} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{SbO}(\text{OH})_2$, a wellknown remedy for Kala-azar, in the treatment of wounds and as a stabiliser for nitro-cellulose, urea is employed. Urea is a softener for cellophane, rayon, etc.

Estimation.—Urea in urine is estimated by adding a known volume of urine to an excess of alkaline hypobromite solution and measuring the volume of nitrogen evolved (*vide* reaction (v) p. 167). This is 7.8% lower than the theoretical though urine contains other compounds which give nitrogen. The method is for rough estimations only.

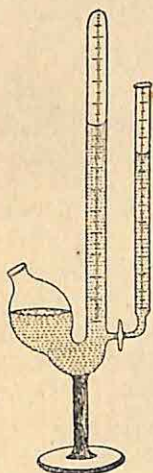


Fig. 41. The ureometer.

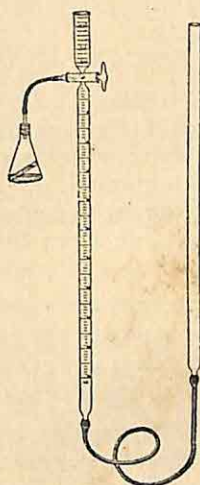


Fig. 42. Lunge's nitrometer.

The large tube closed at upper end (Fig. 41) is filled with freshly prepared hypobromite solution (10 c.c. of bromine and 56 g. of caustic potash in 100 c.c. of water). In the side-tube is taken urine or a dilute urea solution. By opening the stopcock, 1 c.c. of urine is introduced into the larger limb. When no more gas evolves, the volume is noted. The closed tube is graduated to indicate the amount of urea per c.c. of solution. Lunge's nitrometer (Fig. 42) may also be employed for this purpose.

Biochemical method.—Urea is quantitatively and selectively decomposed into ammonium carbonate by urease (p. 267). The experimental arrangement is shown in Fig. 43. The tube (A) contains water which retains any trace of ammonia in the air drawn through the apparatus. In (B) is placed 5 c.c. of urine, 10 c.c. of soya-bean extract, 5 c.c. of phosphate buffer (pH 8.0) and a little liquid paraffin to prevent frothing. It is placed in a beaker of water kept at $50^\circ\text{--}60^\circ$. The tube (C) contains 25 c.c. of 0.02N HCl. The tubes are closed as soon as urease is added and allowed to stand for 15 minutes. By means of a water pump, a slow current of air is drawn through the system. Any ammonia formed in the second tube is

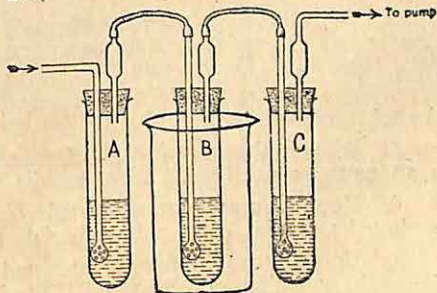
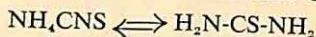


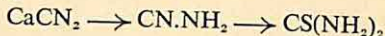
Fig. 43. Estimation of urea with urease.

absorbed in the third. 5 g. of solid pot. carbonate is added to the second tube to set free any combined ammonia which likewise is swept into the third tube. The acid in (C) is estimated, the amount of ammonia liberated is thus known. Traces of heavy metals inhibit the reaction.

Thio-urea, thio-carbamide, $\text{H}_2\text{N-CS-NH}_2$, is made by heating ammonium thiocyanate, NH_4CNS , (a by-product in the wet purification of coal-gas) to 170° (cf., formation of urea from ammonium cyanate, p. 265), extracting the residue with water and crystallising the product.

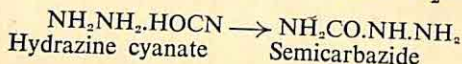


It is also manufactured from calcium cyanamide by treating with dilute H_2SO_4 , filtering off CaSO_4 , adding excess NH_4OH to the filtrate and passing H_2S gas.

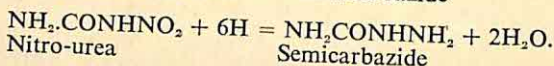


Thio-urea is a colourless, crystalline solid (m.p. 180°), fairly soluble in water and alcohol. It is made into synthetic plastics which are more stable and more water-resistant than urea plastics. Like urea it behaves as a tautomeric compound, giving both N-alkyl and S-alkyl derivatives. Thio-urea is a reagent for the estimation of lead and cadmium. It protects wool and furs from insects.

Semicarbazide, $\text{NH}_2\text{CONHNH}_2$, is made by the interaction of hydrazine sulphate and potassium cyanate (cf., preparation of urea from ammonium sulphate and potassium cyanate, p. 265). It may also be prepared by the electrolytic reduction of nitro-urea, $\text{NH}_2\text{CONHNO}_2$ (obtained by adding solid urea nitrate to conc. H_2SO_4 at -3°).



Hydrazine cyanate Semicarbazide



Nitro-urea

Semicarbazide

Semicarbazide (the half amide half hydrazide of carbonic acid) is a crystalline solid (m.p. 96°), soluble in water and alcohol. It is a fairly strong base; the sulphate or hydrochloride is widely used as a reagent for aldehydes and ketones (pp. 129, 139).

QUESTIONS

1. Why urea is called carbamide? Mention two experiments which support this view of its composition. Explain the reactions used in its detection. B.Sc. Pass, 1938, Dacca Uni.
2. How is carbonyl chloride prepared? Describe the action of water, alcohol, and ammonia on it. How is it related to carbonic acid?
3. Discuss the constitution of urea. How could you detect its presence in an aqueous solution? What are its uses?
4. How is urea best estimated? Give a neat sketch of the apparatus employed and also discuss the principle involved in its estimation.
5. How is urea commonly prepared? Give its important reactions, and discuss its constitution. B.Sc. 1934, Punjab Uni.
6. How is urea manufactured? Discuss its structure. What happens when it is heated? How does it react with (a) nitrous acid, (b) alkaline hypobromite, and (c) malonic ester? B.Sc. Degree Exam. 1942, Andhra Uni.

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CHAPTER XXVII

THE CARBOHYDRATES

A very important group of natural products consisting of carbon, hydrogen and oxygen, has the name *carbohydrate*. The last two elements occur in the ratio 2:1 as in water. Their general formula may, therefore, be represented by $C_xH_yO_y$, or $C_x(H_2O)_y$, whence the name 'carbohydrate' or hydrate of carbon. This is somewhat misleading, for

(1) These compounds do not behave like hydrates of other elements and in fact, no hydrate of carbon is known.

(2) Compounds other than carbohydrates may have the same general formula, such as formaldehyde, CH_2O ; lactic acid, $C_3H_6O_3$; acetic acid, $C_2H_4O_2$; methyl formate, $C_2H_4O_2$; inositol, $C_6H_{12}O_6$, etc.

(3) Some carbohydrates do not contain hydrogen and oxygen in the same ratio (2:1) e.g., rhamnose and fucose have the molecular formula, $C_6H_{12}O_5$, while digitoxose is $C_6H_{12}O_4$.

Nevertheless, the name has been retained for want of a more suitable one. Carbohydrates are important both from biochemical and industrial points of view. It has been estimated that they constitute about three-fourths of the dry weight of the plant world. They include:

(i) **Sugars**, e.g., cane-sugar, glucose, etc.; some of these are important articles of food, and the sources of alcohol, etc. They make fruits sweet.

(ii) **Starches** such as rice, wheat, potato, barley, etc., which are by far the most important food-stuffs.

(iii) **Celluloses** in the form of cotton, jute, straw, grass, wood, etc. These supply textiles, paper, etc.

Some of the most useful materials for our existence and civilisation are obtained from carbohydrates. They are, in fact, the fuel which serves to carry on the vital processes. Carbohydrates occur most abundantly in plants and only to a limited extent in animals (as milk-sugar, glycogen, etc.). About 40 sugars have so far been isolated from these sources. It is a fascinating problem for the plant-physiologist to explain how these complex bodies are synthesised by plants from simple substances like carbon dioxide and water. What rôle they play in human metabolism, it is not within our domain to discuss. We shall discuss their chemistry only.

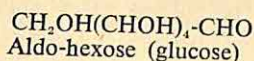
Classification.—The carbohydrates may be broadly subdivided into two groups, *viz.*, *sugars* and *non-sugars*. The sugars such as glucose, cane-sugar, etc., are soluble in water, sweet to the taste and crystalline; while non-sugars, e.g., starch, cellulose, etc., are insoluble, practically tasteless and apparently amorphous. But a more scientific classification is based on their molecular composition, e.g.,

(i) *Monosaccharides* or monosaccharoses (Greek *sakkharon*, sugar) which include carbohydrates up to nine carbon atoms in the molecule, such as xylose, $C_5H_{10}O_5$; glucose, $C_6H_{12}O_6$, etc.

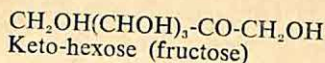
(ii) *Di-, tri- and tetrasaccharides* which contain twelve, eighteen or twenty-four (i.e., multiples of six) carbon atoms, such as cane-sugar, $C_{12}H_{22}O_{11}$, raffinose, $C_{18}H_{32}O_{16}$, stachyose, $C_{24}H_{42}O_{21}$. These may be regarded as glucosides of sugars, as glucose is invariably a common constituent. They are also collectively called *oligosaccharides* (*oligo*, a few). These yield 2, 3 or 4 mols of monosaccharides on hydrolysis.

(iii) *Polysaccharides* such as starch, cellulose, glycogen, etc., which are of large but unknown mol. wts. and represented by the general formula $(C_6H_{10}O_5)_n$. They are formed by condensation from n molecules of monosaccharoses by the elimination of n molecules of water. They yield many monosaccharide mols. on hydrolysis. Pentosans like xylan and araban, $(C_5H_8O_4)_n$, belong to this group. Along with cellulose, they are widely distributed in nature. Plant gums and mucilages, widely used as adhesives and thickening agents, are hetero-polysaccharides; e.g., *gum arabic* consists of arabinose, rhamnose, galactose and glucuronic acid units. *Agar*, a laxative and a culture medium in microbiology, is the sulphuric acid ester of galactan, a linear polymer of galactose. It is a seaweed colloid extracted from *Gelidium*.

Monosaccharoses are polyhydric alcohols having a free or potential aldehyde or keto group. They are the simplest of carbohydrates and are non-hydrolysable. The names of carbohydrates end in *-ose*. The monosaccharides are further subdivided according to the length of their carbon chain, e.g., pentose, $C_5H_{10}O_5$, hexose, $C_6H_{12}O_6$, etc. Of these, the most important are the hexoses, $C_6H_{12}O_6$. They mostly occur free in nature and are called aldoses or ketoses according as they contain the aldehyde or the ketone group. Thus, glucose is an aldo-hexose, and fructose a keto-hexose:



Aldo-hexose (glucose)



Keto-hexose (fructose)

General properties.—The monosaccharides or monoses are generally crystalline, neutral bodies, insoluble in ether, sparingly soluble in alcohol and readily soluble in water. They are sweet to the taste, and char when heated. Naturally occurring monosaccharides are optically active, their specific rotation helps their identification. Carbohydrates, as a rule, are remarkably stable to racemisation (p. 260).

As alcohols, sugars form both ethers and esters. Methylation is usually done with methyl iodide and silver oxide, or dimethyl sulphate and alkali, and acetylation with acetic anhydride and $ZnCl_2$. Methylated and acetylated sugars have proved useful in the elucidation of their configuration. Both aldoses and ketoses readily reduce ammoniacal solution of silver nitrate and Fehling's solution. The latter serves as a method for the estimation of sugars. The ketoses thus differ from ordinary ketones which are *not* reducing. The monosaccharides form additive compounds with HCN , but do not yield aldehyde-ammonias or bisulphite compounds. Both aldoses and ketoses, however, produce oximes, hydrazones, phenylhydrazones, etc. The phenylhydrazone first formed further reacts with two more molecules of the reagent, as we shall see shortly, to produce sparingly soluble, yellow *osazones* which have characteristic crystalline shapes (Fig. 44) and definite melting points. These serve for the identification (and in some cases separation) of the sugars. Emil Fischer (1852-1919), the celebrated German

chemist, to whom a fair portion of our knowledge of sugar chemistry is due, first introduced this valuable reagent which he discovered in 1875.

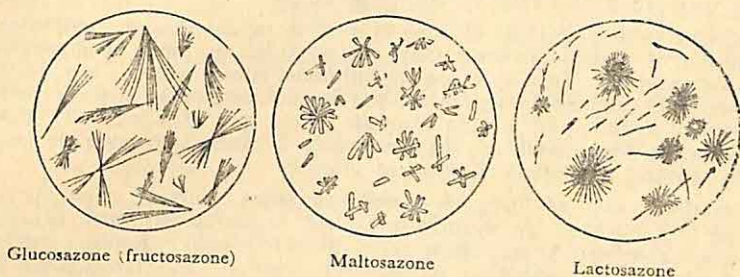
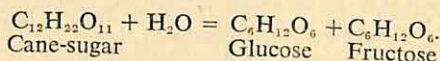


Fig. 44. Crystals of osazones.

Aldoses are readily oxidised by mild oxidising agents to monocarboxylic acids and, by strong nitric acid, to dicarboxylic acids, both containing the *same* number of carbon atoms. Ketoses, on oxidation, yield acids with a *fewer* carbon atoms. Hexoses, but *not* pentoses, undergo alcoholic fermentation with yeast (p. 87). On reduction with sodium amalgam, both aldoses and ketoses take up two atoms of hydrogen and form corresponding alcohols. With hot and concentrated alkalis, sugars turn brown and ultimately resinify; with warm *dilute* alkalis isomerisation may take place; glucose thus partially changes to fructose. Monosaccharides form metallic derivatives with lime-, strontia- and baryta-water; some of these, being sparingly soluble in water, are useful in purifying sugars. Distilled with moderately strong HCl, pentoses yield furfural, $C_5H_4O_2$, (which gives an intense violet-red coloration with aniline acetate) and hexoses form hydroxymethylfurfural which readily passes on to lævulinic acid (p. 199). Pentoses can thus be distinguished from hexoses. By condensing the furfural with phloroglucinol in HCl, pentoses are usually estimated.

d-Glucose, grape-sugar or dextrose, $C_6H_{12}O_6$.—By far the most important monosaccharide is glucose (Greek *glucus*, sweet) which is widely distributed in the seeds and leaves of plants. Together with fructose, it occurs in large quantities (20-30%) in ripe grapes (hence the name grape-sugar), sweet fruits, the nectar of flowers, the white and yolk of egg, and in our blood in small quantities. Honey is a mixture of glucose and fructose (1:1) in water (20%). Glucose is produced in our system by the hydrolysis of cane-sugar and starch mainly:



Both cellulose and starch, on hydrolysis, finally yield glucose. Other intermediate products are usually formed in either case:

Cellulose $\rightarrow$ cellodextrin $\rightarrow$ cellobiose $\rightarrow$ glucose

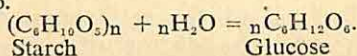
Starch $\rightarrow$ dextrin $\rightarrow$ maltose $\rightarrow$ glucose

All disaccharides and most glucosides have glucose as one of their constituents. Anthocyanins—the water-soluble colouring matters of many plants and flowers—are also glucosides. Some tannins are esters of glucose and hydroxy-aromatic acids.

Normally, 0.08 to 0.11% glucose is present in our blood, and none in urine. Blood of diabetic patients may contain 0.3% or more of glucose and urine as high as 10%. *Insulin*, a protein hormone, effects more or less complete decomposition of glucose in the body, and is administered to diabetic patients whose normal secretion of insulin into the blood has been seriously affected due to defective functioning of the pancreas. Fructose, however, is readily utilised by diabetic animals in contrast to glucose.

Preparation.—40 g. of finely powdered cane-sugar, 4 c.c. of conc. HCl and 100 c.c. of 90% alcohol are warmed in a flask to about 50°, with occasional shaking, for about two hours. It is then allowed to cool. A few crystals of anhydrous glucose are added to induce crystallisation, and the mixture kept at room temperature, when glucose, being less soluble in alcohol than fructose, crystallises first. It is filtered off and purified by recrystallisation from 80% alcohol.

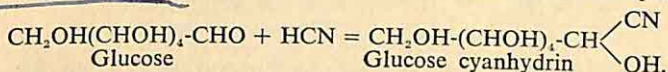
Manufacture of glucose.—Though cellulose can be almost quantitatively hydrolysed to glucose, the process being lengthy and tedious, is seldom commercially followed. It is, however, reported that in Soviet Russia, the difficulties of such large-scale production have been overcome. Glucose is manufactured by hydrolysing starch with dilute mineral acids. Rice, maize or potato is mixed with sufficient water (about 3 times by weight) and heated under pressure (4.5 atmospheres) with dilute sulphuric or hydrochloric acid (0.5%). The hydrolysis is complete in about 1½ hours. The product is neutralised with soda ash. The filtered solution is decolorised by passing through bone-char filters and concentrated in vacuum pans. The product solidifies on cooling. It is sold in small slabs or as a syrup. Commercial glucose (also called *corn sugar*) always contains some maltose and dextrin. The pure form may be obtained by crystallisation from methyl alcohol. Unlike cane-sugar, glucose is rather difficult to crystallise. Manufacture of glucose is quite a big industry in many countries but not in India. India imported 10,203,990 lb. of glucose worth Rs. 40,08,662 in 1955-56.



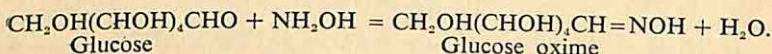
Properties.—Glucose is a white, crystalline solid, sweet to the taste (but less sweet than cane-sugar) and readily soluble in water. From aqueous solution, it crystallises in plates with one molecule of water, which melt at 83°. From alcohol, the anhydrous crystals (m.p. 148°) are obtained. Glucose is dextro-rotatory, hence the name *dextrose*; but l-glucose is also known. The specific rotation of a freshly prepared solution of glucose in water is $[\alpha]_D = +110^\circ$. The value falls gradually and finally becomes $[\alpha]_D = +52.5^\circ$. This change in rotation is accelerated by heat and alkalis. If, however, glucose is crystallised from dry pyridine, its rotation in freshly prepared aqueous solution is $[\alpha]_D = +19^\circ$. On standing, the value becomes $[\alpha]_D = +52.5^\circ$. This shift in optical activity is known as *mutarotation* (Latin *mutare*, to change). Many sugars exhibit mutarotation. It is because glucose exists in two stereoisomeric forms, viz., α -d-glucose (from alcoholic or acetic acid solution) and β -d-glucose (from pyridine solution). In aqueous solution, the α -form changes to the β - and *vice versa* until equilibrium is reached, the mixture having the rotation $[\alpha]_D = +52.5^\circ$. It contains about 34% of the α - and 66% of the β -form

(i.e., in the ratio 1: 2 approximately). Ordinary glucose is mainly the α -variety. A sugar exhibits mutarotation in a solvent such as water. A laevo-rotatory and also an inactive variety of glucose have been synthesised. Chemically, glucose behaves both as an aldehyde and an alcohol. For convenience, it is represented here by an open-chain though, in fact, it has a ring structure.

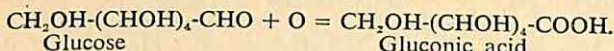
Reactions of glucose.—(i) It reacts with HCN and forms the cyanhydrin :



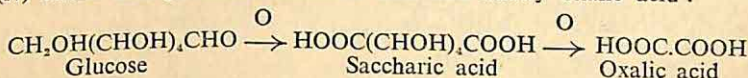
(ii) With hydroxylamine, it gives the oxime :



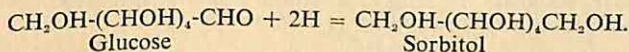
(iii) Chlorine- or bromine-water oxidises it to gluconic acid (m.p. 131°) :



(iv) Nitric acid produces saccharic acid and finally oxalic acid :



(v) Sodium amalgam, electrolytic reduction or sodium borohydride gives sorbitol :

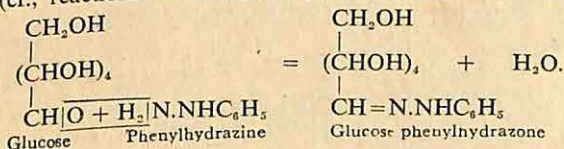


Hydriodic acid and red phosphorus reduce glucose at 100° to 2-iodohexane and ultimately to *n*-hexane.

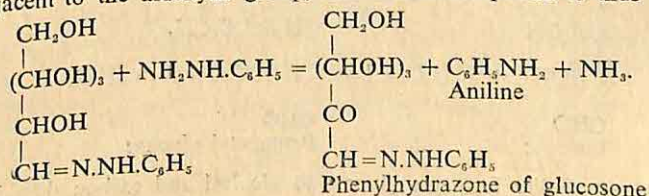
(vi) Phenylhydrazine finally produces an osazone (-ose + hydrazone).

Dissolve 1 g. of phenylhydrazine in 1 c.c. of glacial acetic acid and dilute it to 10 c.c. with water. Add 0.5 g. of glucose in 5 c.c. of water to the phenylhydrazine solution. Warm the mixture in a water-bath, yellow crystals of osazone (m.p. 204°) appear after about 8 minutes. It may be recrystallised from alcohol. The reaction takes place as follows :

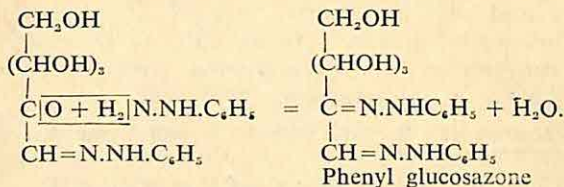
(a) Glucose and phenylhydrazine first give glucose phenylhydrazone as usual (cf., reactions of aldehydes, p. 129), which is soluble in water.



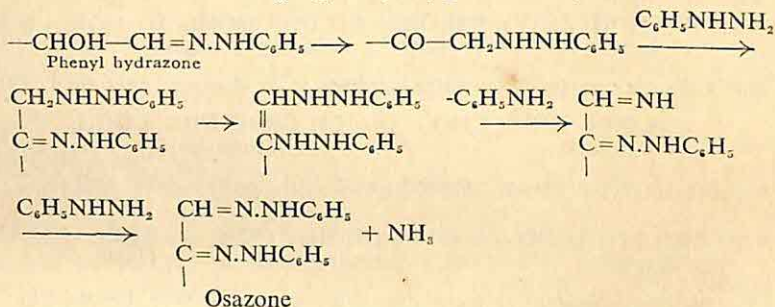
(b) A second molecule of phenylhydrazine then 'oxidises' the -CHOH-group adjacent to the aldehyde group, and a keto-compound is thus formed :



(c) This keto group reacts with a third molecule of phenylhydrazine to give insoluble phenyl glucosazone (cf., reactions of ketones, p. 138).



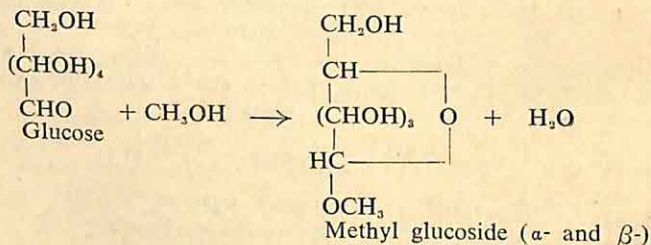
It is now believed that osazone is formed as follows for phenylhydrazine is not an oxidising agent (Weygand, 1940):



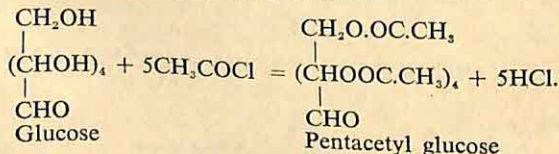
The osazone stabilises by ring formation due to hydrogen bonding and no further reaction with phenylhydrazine is possible.

(vii) Fehling's solution or ammoniacal silver nitrate is readily reduced by glucose (cf., behaviour of aldehydes, p. 130).

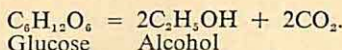
(viii) With absolute methyl alcohol, glucose forms two glucosides in presence of dry HCl. Apparently, the aldehyde (but in fact an -OH) group combines with the alcohol. These glucosides exhibit no aldehydic function or mutarotation. They are ethers and so, fairly stable compounds. 'Glucoside' is a general term for any sugar having a substituent on carbon-1.



(ix) With acetyl chloride or acetic anhydride, the pentacetyl derivative is finally obtained as from polyhydric alcohols:



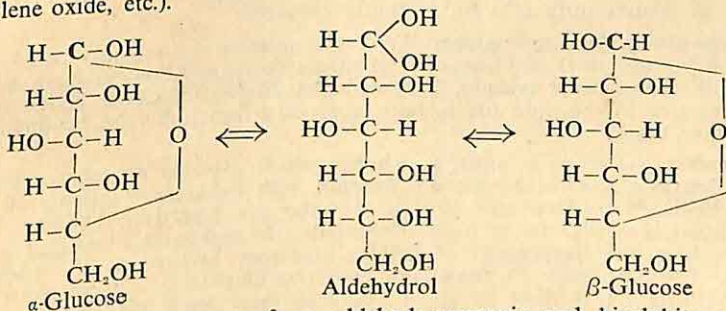
(x) Yeast readily ferments glucose to alcohol and carbon dioxide (p. 87).



(xi) With lime-water, calcium glucosate, $\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{CaO}$, (soluble in water but insoluble in alcohol) is formed. This is decomposed by carbon dioxide to pure glucose. With baryta-water, a similar compound is obtained. Glucose is more acidic ($k_a = 6.6 \times 10^{-12}$) than a monohydroxy alcohol.

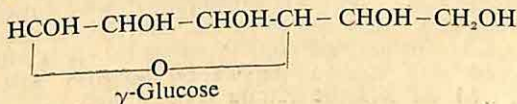
Constitution of glucose.—(i) The molecular formula for glucose, from analytical data, is $\text{C}_6\text{H}_{12}\text{O}_6$. (ii) On acetylation, it gives a penta-acetyl derivative, and on methylation, a penta-methyl ether. Hence, glucose has five alcoholic -OH groups. These are presumably linked to five carbon atoms as glucose is a stable compound. (iii) On oxidation, it gives gluconic acid, $\text{C}_6\text{H}_{12}\text{O}_7$. It is reducing and reacts with HCN , $\text{C}_6\text{H}_5\text{NHNH}_2$, NH_2OH , etc., hence an aldehydic group is present. (iv) Sodium amalgam reduces glucose to sorbitol, $\text{C}_6\text{H}_{14}\text{O}_6$, (a hexahydric alcohol) which, with HI , gives normal β -iodohexane, $\text{CH}_3\text{CHI}(\text{CH}_2)_4\text{CH}_3$. Glucose cyanhydrin, on hydrolysis and reduction with HI , gives normal heptylic acid, $\text{CH}_3(\text{CH}_2)_5\text{COOH}$. So carbon atoms in glucose apparently form a straight chain. To explain these facts, Baeyer in 1870 suggested $\text{CH}_2\text{OH} \cdot \text{CHOH} \cdot \text{CHOH} \cdot \text{CHOH} \cdot \text{CHOH} \cdot \text{CHO}$ for glucose, which was established by Kiliani in 1886.

This has four asymmetric carbon atoms, so 2^4 , i.e., sixteen optical isomers should exist according to van't Hoff but actually there are more. The above constitution fails to account for this, and (i) mutarotation, (ii) its failure to form sodium bisulphite compound or aldehyde-ammonia, and (iii) the existence of two isomeric methyl glucosides, or of α - and β -D-glucose. Emil Fischer discovered the two methyl glucosides in 1894. Tollens (1883) first suggested a butylene oxide ring formula for glucose. In 1926, Haworth proved that glucose has a six-membered amylene oxide ring. (When compounds other than acids form rings with oxygen, they are called oxides; e.g., ethylene oxide, amylene oxide, etc.).

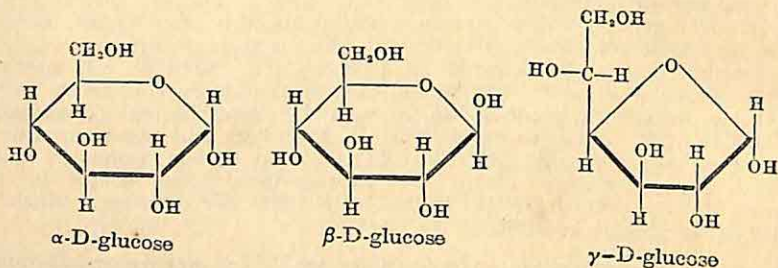


Inability of glucose to form aldehyde-ammonia and bisulphite-compound is thus explained—glucose has a potential, but not free aldehyde group. The characteristic band for the aldehyde group is absent in the ultra-violet absorption spectrum of glucose in aqueous solution. Further, the aldehydic carbon (in thick type) has now become asymmetric and the spatial arrangement of H and -OH has given rise to two additional stereoisomers, viz., α - and β -glucose. Mutarotation as well as the formation of two methyl glucosides is also accounted for. The oxide ring is not very stable; with strong reagents, it opens up readily and exhibits aldehydic reactions. α -Glucose is converted to the β -form through the open-chain, hydrated aldehyde (aldehydrol) form.

There is a third glucose, called γ -glucose, with a five-membered ring. It is unstable and known only in the form of derivatives, e.g., γ -methylglucoside, obtained as a syrup by treating D-glucose in the cold with methanol containing 1% dry HCl.



Haworth represents glucose by a hexagonal or pyranose structure which has been generally accepted. α - and β -glucose have the same structure but different configurations; γ -glucose has a different structure and configuration. Compounds with two -OH groups lying close to one another in space, e.g., glycerol but not ethylene glycol, increase the electrical conductivity of boric acid considerably. Of the two stereoisomers of glucose, the one that behaves likewise, is called α -, in which -OH groups on carbon 1 and 2 are on the same side of the plane of the ring.



Uses.—Glucose is extensively used in confectionery, preservation of fruits, making jams and silvering mirrors. Mixed with vitamin D and calcium, it forms food for the invalid. Glucose is injected intravenously for increasing blood-sugar. It is fermented to wine and beer. A commercial synthesis of vitamin C (l-ascorbic acid—an unsaturated sugar derivative) starts from d-glucose. India requires 90,000 lb. of it annually of which only 500 lb. is made locally.

Detection.—(i) Glucose reduces Fehling's solution (commonly used for detecting sugar in urine) and ammoniacal silver nitrate solution, giving a silver mirror. (ii) The osazone (vide p. 275) melts at 204°. (iii) Conc. H_2SO_4 does not char glucose in the cold (distinction from cane-sugar), but on heating, the solution turns black.

Estimation.—Glucose in aqueous solution which contains no other reducing agent, is determined volumetrically by titration with Fehling's solution. 10 c.c. of fresh Fehling's solution and 40 c.c. of water are heated to boiling. The sugar solution is slowly run in from the burette, the end-point is reached when the blue colour just disappears. Methylene blue may be used as an end-point indicator. The blue colour is discharged by excess glucose. To avoid oxidation by air, the titration is done at about 100°, so that steam fills up the flask. Fehling's solution is standardised against a known glucose solution in the same way. For quick estimations, cuprous oxide from a known volume of liquid with Fehling's solution, is weighed. Glucose in urine is thus estimated.

Synthesis of glucose.—Emil Fischer reduced α -acrose (fructose, p. 114) to mannitol which he oxidised with HNO_3 to mannonic acid. This, on epimerization, gave gluconic acid which was reduced to glucose.

Fructose, fruit-sugar or laevulose, $\text{C}_6\text{H}_{12}\text{O}_6$, occurs with glucose, in fruits (hence the name, fruit-sugar) and honey. Cane-sugar, on hydrolysis, yields fructose and glucose (p. 273). Inulin, $(\text{C}_6\text{H}_{10}\text{O}_5)_n$, found in some plants, is a polymer of fructose.

Preparation.—In the laboratory, fructose is prepared by hydrolysing cane-sugar with dilute H_2SO_4 . The acid is neutralised with barium carbonate and the filtrate concentrated. It is cooled in ice, and slaked lime is slowly added; calcium fructosate, being sparingly soluble, separates. It is filtered, washed with water and treated with carbon dioxide in aqueous suspension. Calcium carbonate is filtered off and the filtrate concentrated. On cooling and after

sowing with a few crystals of pure fructose to induce crystallisation, the crystals slowly appear. Fructose and its derivatives crystallise much less readily than glucose.

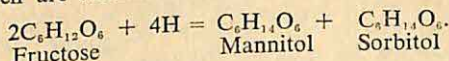
Fruit-sugar is manufactured from *inulin* which occurs in the tubers of dahlia and Jerusalem artichoke. Inulin is heated with dilute sulphuric acid for about an hour. The hydrolysis is practically quantitative; the acid is removed by baryta. On concentrating the solution under reduced pressure, crystals of fructose slowly appear, which may be purified by re-crystallisation from hot, absolute alcohol. Inulin is also hydrolysed by water under pressure containing carbon dioxide.

Properties.—Fructose forms rhombic crystals (m.p. 102° – 104°) from absolute alcohol. From water, we get $2C_6H_{12}O_6 \cdot H_2O$. It closely resembles glucose but is *lævo*-rotatory; hence the name *lævulose*. A *dextro*-rotatory *lævulose* is also known. Fructose is sweeter and also more hygroscopic than glucose; in fact, it is the sweetest of all sugars. It is fermented by yeast to alcohol and carbon dioxide but less readily than glucose. It exhibits mutarotation—the sp. rotation is $[\alpha]_D = -133^{\circ}$ immediately after dissolving, and $[\alpha]_D = -92^{\circ}$ finally. Fructose is not oxidised by bromine-water.

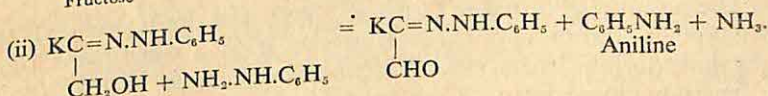
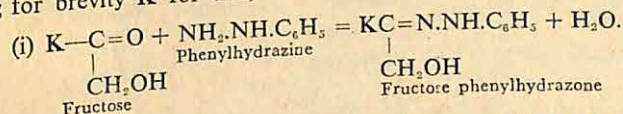
Reactions.—Unlike ordinary ketones, fructose readily reduces ammoniacal silver nitrate and Fehling's solution like glucose. This is due to the easily oxidisable group $-CO \cdot CH_2OH$ in the molecule. Nitric acid or bromine-water oxidises fructose to mesotartaric and glycollic acid; glucose, on oxidation, gives saccharic acid (p. 275).



This suggests the presence of a ketone group. Fructose forms a cyanhydrin, an oxime, etc. On reduction, fructose yields equal amounts of mannitol and sorbitol (which are stereoisomers) but glucose gives only sorbitol.

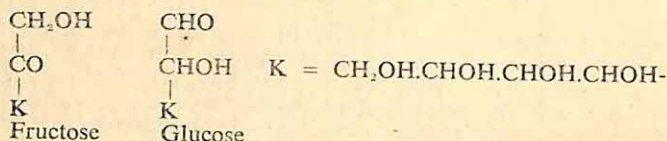


Because with phenylhydrazine it gives the same osazone as does glucose, $CH_2OH \cdot CHOH \cdot CHOH \cdot CHOH \cdot$ is common to both glucose and fructose. Putting for brevity K for this,

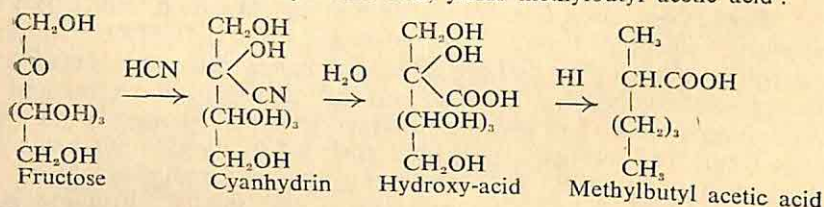


Constitution.—(i) From analytical data, fructose is $C_6H_{12}O_6$. (ii) It forms a penta-acetyl derivative on acetylation, so it has five $-OH$ groups; and possibly not more than one $-OH$ linked to the same carbon atom. (iii) On oxidation with HNO_3 , it yields acids with a fewer carbon atoms e.g., tartaric and glycollic acids; it reacts with HCN , $C_6H_5NH \cdot NH_2$, etc. Hence, it has a

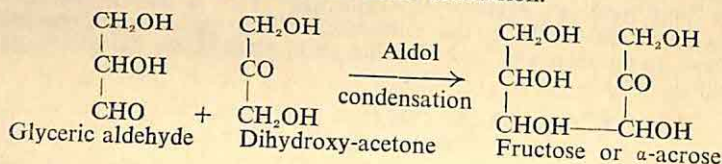
keto group. (iv) Fructose and glucose yield the same osazone. The two carbon atoms, where they differ, have the following arrangement.



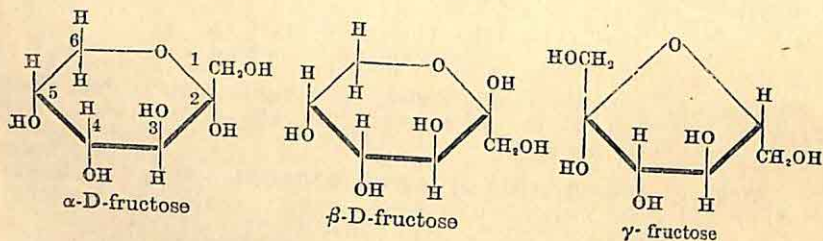
(v) Fructose cyanhydrin, on hydrolysis, gives the corresponding hydroxy-acid which, on reduction with hydriodic acid, yields methylbutyl acetic acid:



The keto group, therefore, occupies the second position from one end. Synthesis of inactive fructose by condensing dihydroxy-acetone and glyceric aldehyde (p. 114) also leads to the same conclusion.



Like glucose, it forms stereoisomeric fructosides. A pyranose structure (with an aylene oxide ring) has been assigned to it.

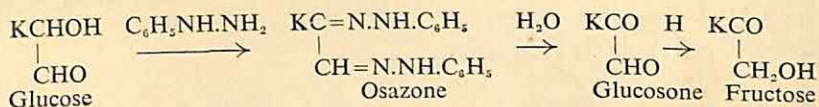


The α - and β -forms of fructose have not been isolated as yet. γ -Fructose is known only as derivatives. It is a constituent of cane-sugar but during hydrolysis, the fructo-furanose is transformed into the fructo-pyranose form. Combined fructose is invariably γ .

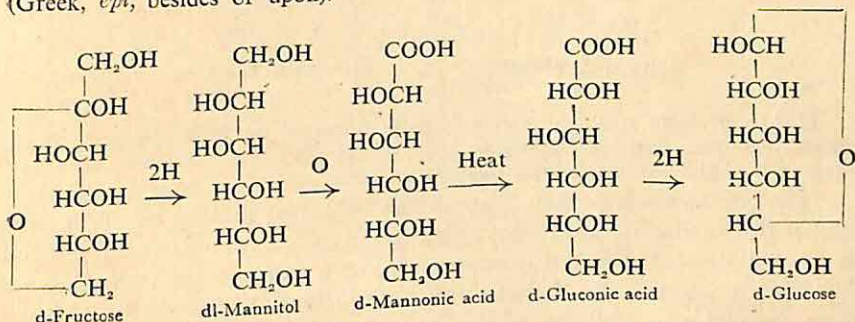
Ordinary fructose has a configuration similar to d-glucose, hence it is sometimes called d-fructose though it is laevo-rotatory. For similar reasons, we may have l-sugars (which are mirror images of d-sugars) that are dextro-rotatory. This system, though somewhat confusing, is generally followed in sugar chemistry. Here d and l evidently refer to the configuration and not to the sign of optical rotation. Some use Roman capital letters, D- and L-, for configuration and italics, *d*- and *l*-, for optical rotation.

Conversion of glucose into fructose and vice versa. Glucose is first transformed into its osazone with phenylhydrazine. The osazone, on hydrolysis,

yields a keto-aldehyde, called osone. The latter, on reduction with zinc dust and acetic acid, gives fructose. Putting K for $\text{CH}_2\text{OH}(\text{CHOH})_2\text{CHOH}$ —



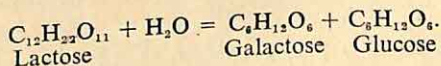
Fructose, on reduction, yields mannitol and sorbitol. Mannitol is oxidised to mannonic acid which is partially converted into gluconic acid by heating with pyridine or quinoline (epimerization). It is then reduced to glucose. Partial or complete inversion of H and OH on carbon-2 is called epimerisation (Greek, *epi*, besides or upon).



Fructose can be distinguished from glucose by its negative rotation and the insoluble lime compound with lime-water, calcium glucosate being soluble in water. Sodium hypiodite oxidises aldoses but not ketoses. So fructose may be estimated in presence of glucose.

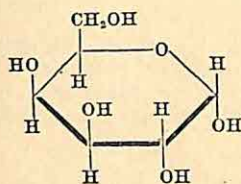
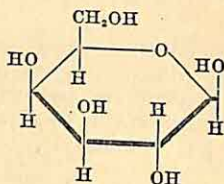
Tests.—(i) Fructose reduces Fehling's solution and ammoniacal silver nitrate. (ii) It yields an osazone (the same as from glucose) which, however, appears after 5 minutes. (iii) Heated with a little resorcinol in HCl, fructose gives a brownish red ppt. All keto-hexoses give this test (Selivanoff's test). (iv) Warmed with a little freshly made ammonium molybdate solution and a few drops of glacial acetic acid, fructose gives a deep greenish blue coloration.

Galactose, $\text{C}_6\text{H}_{12}\text{O}_6$, rarely occurs free in nature; *galactan*, a polymer of galactose, is found in many plants and in sea-weeds (e.g., agar or agar-agar). It is a constituent of lactose or milk-sugar from which Pasteur (1856) first isolated it, whence its name (*Gala*, milk). As galactoside, it occurs in some plants (e.g., digitalin) and in combined state in brain and nerve tissues, hence called brain sugar. Galactose is prepared by hydrolysing lactose with boiling dilute H_2SO_4 and separating it from glucose by fractional crystallisation from water. Galactose crystallises first.



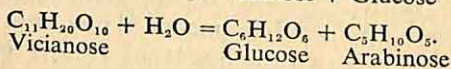
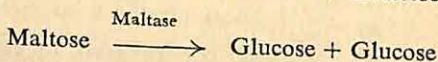
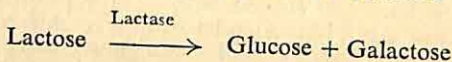
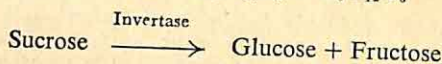
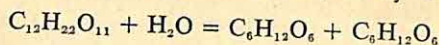
Galactose forms prisms with one molecule of water (m.p. 119°); the anhydrous sugar melts at 166° . Galactose, an aldose, exhibits mutarotation. It is dextro-rotatory $[\alpha]_D = +80.3^\circ$ (final value); $[\alpha]_D$ for α -galactose is $+145^\circ$ and for β - $+54^\circ$. It is less sweet and less soluble in water than its isomers, glucose and fructose. Galactose resembles glucose. It is slowly fermented by yeast. On reduction, it yields dulcitol, a hexahydric alcohol, which is inactive. On oxidation,

galactonic and finally, mucic acid (which are isomeric with gluconic and saccharic acid respectively) are obtained. It forms an osazone (m.p. 194°, separates after 30 mins.), reduces Fehling's solution and gives a penta-acetyl derivative.

 α -D-galactose β -D-galactose

There are many synthetic sugars—mostly prepared by Emil Fischer. These include pentoses, hexoses, heptoses, etc., many of which are not found in nature, e.g., l-glucose, d-fructose, l-galactose, etc.

The disaccharides are 'anhydrides' of two molecules of monosaccharides, same or different. Glucose is a common constituent of all known disaccharides, the other may be a pentose or a hexose, an aldose or a ketose. By far the most important disaccharide is cane-sugar or sucrose. Milk-sugar (or lactose) and malt-sugar (or maltose) are isomeric with cane-sugar. These are readily hydrolysed to constituent sugars on boiling with dilute acids, or by enzymes.



Disaccharides are sweet, crystalline bodies, soluble in water. They are not usually fermented by yeast unless hydrolysed. They crystallise more readily than monosaccharides. One potential aldehyde or ketone group is invariably occupied in combination, the other may or may not be free. In the former case, disaccharides are reducing, and also exhibit mutarotation.

Sucrose, cane-sugar or saccharose, $C_{12}H_{22}O_{11}$, occurs in many plants, abundantly in sugar-cane. Sugar-maple, sorghum, and some species of palm also contain sucrose. It is found, often with monosaccharides, in many fruits; pine-apple contains about 11%, apricot nearly 6%, ripe banana 5% of sucrose (Latin *saccharum*, sugar cf., Sanskrit *Sarkara* for sugar).

Cane-sugar was known to the ancient people. In India, sugar-cane was cultivated and sugar exported to Europe after Alexander's invasion in 327

B.C. The Greek physicians called it 'Indian salt'. In Europe, honey was the only sweetening material prior to that. In the 19th century cane-sugar became an article of commerce. In 1747 Marggraf, a German chemist, discovered sucrose in beet-root. The sugar content was then only about 6%, it was not an economic source. Agricultural research raised the figure to 18-20%, and in some cases, 28%. The manufacture of sugar from sugar-cane (in India) or beet (in Europe) is one of the most important industries of the world. Beet-sugar and cane-sugar are identical.

Manufacture of beet-sugar.—Beet-roots are washed with water to remove the adhering dirt and mechanically cut into thin slices. These are treated in a series of vats with water at about 90°. The sugar and other crystalloids pass out of the semi-permeable cell wall, and the colloids such as albumin, etc. remain inside due to dialysis. The pulp retains about 0.2% sucrose. The aqueous extract containing 12-15% sugar is heated to 85-90° with 2-3% of lime for about 2 hours. Lime neutralises and precipitates as calcium salts the free acids (oxalic, phosphoric, citric, etc.) which hydrolyse sucrose. Lime coagulates proteins and removes much colouring matters. A part of the lime forms calcium saccharate with sucrose. Excess of lime is removed with carbon dioxide which decomposes calcium saccharate. Calcium carbonate is removed by filter press. The solution is kept slightly alkaline. Sometimes sulphur dioxide is passed in to decolorise the solution. The filtered juice is evaporated in vacuum pans heated by steam. The concentrated liquid is cooled, crystals of sucrose formed are separated from the dark brown mother liquor by centrifuging. The brown raw sugar is refined by filtering its aqueous solution through animal charcoal beds and crystallisation in vacuum pans. From the molasses, a second crop of crystals is recovered in the same way. The molasses (which normally contains about 50% of fermentable sugar) is fermented to alcohol or used as cattle food (it is rich in nitrogen). Most of the sucrose of molasses can, however, be recovered by treating it with hot strontium saccharate formed is removed and strontium hydrate. The recovery of sucrose from the beet is decomposed by carbon dioxide. The recovery of sucrose from the beet is nearly 88%. About 1/3 of the world-production of sucrose is from beet and the rest from cane.

Manufacture of cane-sugar.—The cane with sucrose content 12-19% (soon after harvest to avoid inversion to non-crystallisable sugar), is placed on a cane-carrier, a continuous apron of steel slots carried on roller chains. There is a set of revolving steel knives at the end of the carrier, running at about 500 revolutions per minute. Here the cane is cut into small pieces to feed the mills. These usually pass through 2-roller crushers and four sets of mills. The major portion of juice is pressed out by the crushers and the first two mills. As extraction becomes difficult in later stages due to low juice content, water, hot or cold, is sprayed over the blanket of the fibrous material, called *bagasse*, to dilute the residual juice and aid further extraction by milling. The process is repeated and practically 90-95% of the sucrose is thus extracted. Intensive milling causes some colloidal matter to pass into the juice. The residual *bagasse*, having about 50% of fibre, is used as fuel for steam-raising and for making *celotex*, a heat insulator board.

The dark raw juice contains about 15% of sucrose and small amounts of glucose, fructose, organic acids, colouring matters, gums, nitrogenous bodies, pectin, etc. in solution, and fine particles of *bagasse* in suspension. It is strained to remove the suspended impurities, limed to pH 7.2, and heated nearly to boiling to help the action of lime and coagulation of albuminoids. The solution is allowed to settle in rectangular tanks called subsiders. The top layer of scum and the muddy sediment at the bottom are separated mechanically. Very often, immediately after liming, the juice is taken into conical tanks from the bottom of which sulphur dioxide is bubbled through. This sulphitation and liming are adjusted to pH 7.0. Sulphitation prevents the oxidation of sucrose to brown matter, coagulates gums and albuminoids more effectively with better grains of calcium sulphite formed; the solution is bleached and it yields white crystals.

The clear juice from the subsidiers is pumped into the evaporator supply tank whence it passes to the multiple-effect evaporator. The juice (about 12°Bé) enters the first body of the evaporator and a syrup of about 60°Bé comes out of the last body. Exhaust steam from the engines of the factory boils the juice in the first body, and the vapour from the first body of the multiple-effect evaporator is used for heating the second body and so on. A vacuum of about 26 inches is maintained. The concentrated syrup is led to pans maintained in vacuum for crystallisation. The rest of the process is the same as in the case of beet-sugar. The crystals are separated from the brown liquor (molasses) by centrifuges and if necessary, a little ultramarine or indanthrene blue is added to mask the brownish colour of the crystals.

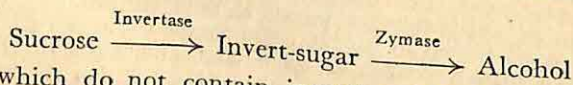
Molasses contains nearly 30% of sucrose; it is consumed by tobacco smokers and used as manure. Alcohol is made from molasses. Poor quality, low yield of cane per acre, and partial recovery of bye-products largely account for the high cost of Indian sugar.

Indian sugar industry.—Prior to 1932-33, there were only 32 sugar factories in India, and practically all the sugar came from Java. In 1918-19, she imported sugar worth £10,409,094. As a result of protection, the number of factories rose up to 158. In 1958, 154 sugar mills produced 20,06,400 tons of white sugar. The recovery of sugar from cane is about 9.5%. In 1958 India exported 50,000 tons of sugar.

Consumption of sugar per annum per capita is 113 lb. in Australia, 103 lb. U.S.A., 37 lb. in Europe, and 25.9 lb. (both unrefined sugar i.e., gur and refined sugar) in India.

Properties.—Sucrose forms colourless monoclinic crystals, soluble in water but practically insoluble in absolute alcohol and ether. It is dextro-rotatory $[\alpha]_D = +66.5^{\circ}$, but exhibits no mutarotation. Pure sucrose melts at 160° to 186° depending upon the medium used for purification. On heating with a little water, it melts and on cooling, solidifies to an amorphous, glassy mass known as *barley sugar*. At 190° - 200° , it loses water and forms a brown product called *caramel*, extensively used in confectionery and colouring medicinal products, wine and beer. At still higher temperature, it carbonises and forms sugar charcoal.

Cane-sugar neither reacts with phenylhydrazine nor reduces. Conc. H_2SO_4 chars it at ordinary temperature. Dilute mineral acids (HCl or HNO_3 is much more effective than H_2SO_4) or certain enzymes hydrolyse it to glucose and fructose, the resulting solution has $[\alpha]_D = -20^{\circ}$. Since dextro-rotatory cane-sugar thus gives a lævo-rotatory mixture, the process is known as *inversion*. Invert-sugar (glucose and fructose) is sweeter than sucrose. It is a substitute for honey, and a food for infants and invalids. A strong sugar solution inhibits the growth of many micro-organisms and is a preservative in jams, etc. Conc. HNO_3 oxidises sucrose to oxalic acid (p. 239). Sucrose is a very weak acid ($k_a = 1.8 \times 10^{-13}$). Lime-water, baryta, etc., form sparingly soluble saccharates with sucrose, e.g., the lime compound is $\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot \text{CaO} \cdot 2\text{H}_2\text{O}$. The strontia compound is utilised in recovering sucrose from beet-molasses. Sucrose is fermented to alcohol by many enzymes:



Yeasts which do not contain invertase (e.g., *Saccharomyces octosporus*), cannot, therefore, ferment sucrose. Moderately strong HCl

converts sucrose into lævulinic acid (p. 199) on boiling. Lævulinic esters, made from sucrose, are solvents for nitrocellulose. Sucrose resists the action of boiling alkalies. With acetic anhydride and sodium acetate, it gives an octa-acetyl derivative.

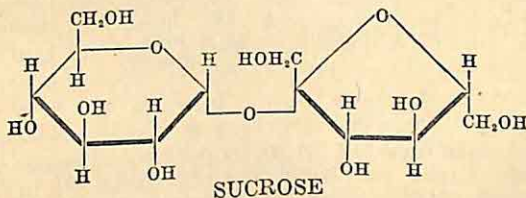
Structure.—(1) From analytical data, sucrose is $C_{12}H_{22}O_{11}$.

(2) On hydrolysis, it readily yields one molecule each of glucose and fructose easily; these are linked through oxygen, and not through carbon.

(3) Sucrose has eight -OH groups as it gives an octa-acetyl derivative.

(4) It is non-reducing and forms no hydrazone, osazone or oxime. Hence the potential ketone and aldehyde groups are occupied i.e., carbon 1 of glucose and carbon 2 of fructose are linked through oxygen.

(5) Octamethylsucrose gives on hydrolysis 2:3:4:6-tetramethyl-d-glucose and 1:3:4:6-tetramethyl- γ -fructose. Therefore, carbon 5 of glucose and of fructose have no -OH group to be methylated. They must have formed rings in the respective hexoses (vide pp. 277, 280). Based on these facts, Haworth (1926) assigned to cane-sugar the structure:



α -Glucopyranose

β -Fructofuranose (γ -fructose)

In sucrose, fructose has a butylene oxide ring which, during hydrolysis, becomes an amylen oxide ring (p. 280). Sucrose has been synthesised in 1944 enzymatically from glucose-1-phosphate and fructose, and by a purely chemical method in 1953.

Tests.—(i) Cane-sugar does not reduce Fehling's solution, but does so after heating with dilute acids (i.e., after inversion).

(ii) The aqueous solution does not darken on warming with caustic soda.

(iii) It chars with conc. sulphuric acid at room temperature.

(iv) Solid sucrose, on heating, turns brown and forms caramel.

(v) The octa-acetate melts at 67° .

Estimation.—(1) Sucrose is estimated by measuring its rotation in aqueous solution (the crude juice is treated with basic lead acetate to precipitate proteins and filtered) with a saccharimeter (a special form of polarimeter showing the sucrose content directly on the scale)—the rotation being proportional to concentration. This is done in sugar factories.

(2) Sucrose is boiled with dilute H_2SO_4 and the invert-sugar estimated with Fehling's solution like glucose (p. 278). Any reducing sugar, if originally present, is similarly determined before inversion.

(3) Pure sucrose may be quickly estimated by a refractometer. the refractive index of an aqueous solution is proportional to its concentration.

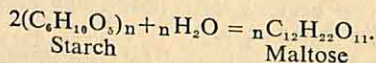
Uses.—By far the largest amount sweetens our food-stuff as table sugar. It is an excellent energy-producing food, giving 1815 calories per lb. Cane-sugar makes soaps transparent. It increases the tensile strength of lime and mortar by 60%. The octa-acetate is a plasticizer for lacquers, and an ingredient of non-aqueous adhesives; it stiffens textiles and makes paper transparent.

Properties of sucrose, glucose and fructose

	Sucrose	Glucose	Fructose
m.p.	160°-186°	148° (anhydrous)	102°-104°
$[\alpha]_D$	+66.5°	+52.5° (final value)	-92° (final value)
	Does not exhibit mutarotation	Exhibits mutarotation	Exhibits mutarotation
Fehling's soln.	Does not reduce	Reduces	Reduces
Nitric acid oxidises to	Oxalic acid	Saccharic acid	Meso-tartaric acid & glycollic acid
With phenylhydrazine	No reaction	Gives phenyl-glucosazone	Gives phenyl-glucosazone
Warmed with am. molybdate	No coloration	Very faint coloration after about 10 mins.	Greenish blue coloration after 3-4 mins.
In ether	Insoluble	Insoluble	- soluble

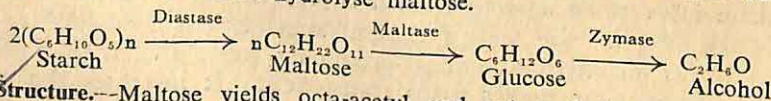
Maltose or malt-sugar, $C_{12}H_{22}O_{11}, H_2O$.—The diastase of germinating barley hydrolyses starch, mainly to maltose (80%). It is thus the main constituent of malt, whence the name. Free maltose occurs in soya-bean. It is an intermediate product in the formation of alcohol from starchy materials (p. 89). Ptyalin of saliva converts insoluble starch into soluble maltose to help digestion. Maltose is easily digested, hence its use as infant and invalid food. It is isomeric with cane-sugar but less sweet. Maltose is a degradation product of glycogen (or animal starch); it is present in beer.

Preparation.—Starch (100 g.) is made into a paste with sufficient hot water and malt extract (6 g.) from germinating barley is added. The mixture is kept for an hour at about 60°, heated to boiling and filtered. The filtrate is concentrated to a syrup on water-bath. Maltose is extracted with 90% alcohol. On evaporating off most of the alcohol, and adding a crystal of maltose, fine needles of maltose separate. The commercial method is similar.



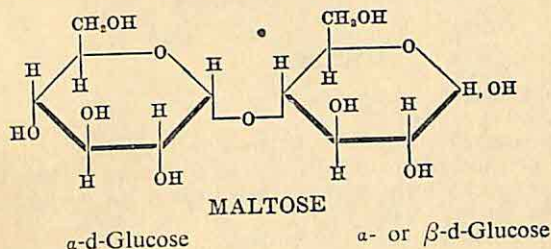
Properties.—Maltose crystallises with a mol. of water in white needles (m.p. 102°). It is very soluble in water but difficultly soluble in alcohol. It is dextro-rotatory, $[\alpha]_D = +130^\circ$ (final value), reducing and exhibits mutarotation. With boiling, dilute H_2SO_4 , as also by maltase, it is hydrolysed to d-glucose only. Unlike cane-sugar, maltose yields an osazone (m.p. 206°) with phenylhydrazine.

Like cane-sugar, maltose undergoes fermentation after hydrolysis. Most yeasts convert it into alcohol because they contain the hydrolytic enzyme maltase. Diastase or invertase cannot hydrolyse maltose.



Structure.—Maltose yields octa-acetyl and octa-methyl derivatives; so it has eight -OH groups. It gives 2 mols. of d-glucose on hydrolysis, which constitute maltose. It is reducing and forms an osazone; the potential aldehyde group is, therefore, free. Maltose, on oxidation, gives maltobionic acid,

$C_{12}H_{22}O_{12}$, so it has only one aldehyde group free. Methyl ester of octamethyl malto-bionic acid yields, on hydrolysis, 2:3:4:6-tetramethyl glucose and 2:3:5:6-tetramethyl gluconic acid. Maltose, on hydrolysis after exhaustive methylation, gives 2:3:4:6-tetramethyl glucose and 2:3:6 trimethyl glucose. Carbon-1 of one glucose and carbon-4 of another, therefore, form the glycosidic linkage. These facts are satisfactorily explained by Haworth's structure :



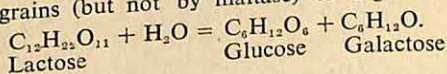
Maltase hydrolyses α -glucosides such as maltose but not β -glucosides, whereas emulsin hydrolyses β -glucosides e.g., cellobiose but not α -glucosides. These are helpful in determining the configuration of glucosides. Malt extract, extensively used in medicine, contains maltose, dextrin and amylolytic enzymes; it has food value and is also a laxative. Malt syrup adds flavour to ice cream, chocolates etc.

Lactose or **milk-sugar**, $C_{12}H_{22}O_{11}$, occurs in the milk of all mammals, hence the name. Cow's milk contains about 4% and mother's milk 6-8%. It has not been found in the vegetable kingdom.

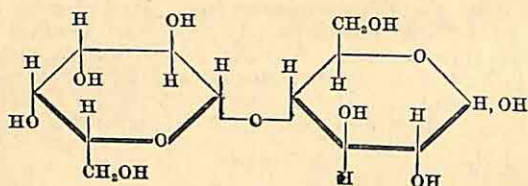
Preparation.—Lactose is commercially made from whey, a bye-product in the manufacture of cheese from milk. The casein of the milk is separated by coagulation with rennet, and the fat by centrifuging. The mother liquor, containing lactose and mineral matters, is concentrated in vacuum pans, crude lactose crystallises. It is decolorised with animal charcoal and recrystallised from water.

Properties.—Lactose forms monohydrate rhombic prisms from water below 93.5° above which β -lactose appears as anhydrous monoclinic crystals. It becomes anhydrous at 130° and melts at 205° with decomposition. It is much less soluble in water than cane-sugar, and insoluble in absolute alcohol or ether. The crystals are hard and small; hence called sand-sugar. Lactose is dextrorotatory, $[\alpha]_D = +55.3^\circ$ (final value) and exhibits mutarotation. By lactic fermentation, it gives lactic acid (p. 189). Ordinary yeast cannot ferment it. *Tarula lactosa* gives ethanol in high yield. Lactose of commerce is the α -form; it is the least sweet sugar.

Constitution.— α -Lactose is readily hydrolysed by dilute acids or lactase found in Kephir grains (but not by maltase) to d-glucose and d-galactose.



It reduces Fehling's solution, exhibits mutarotation, and forms an osazone (m.p. 200°). With conc. HNO_3 lactose gives saccharic and mucic acid. Bromine-water oxidises it to lacto-bionic acid, $C_{12}H_{22}O_{12}$. So lactose, like maltose, has only one potential aldehydic group free. Lactose is a stereoisomer of maltose which it closely resembles. Lactobionic acid, on hydrolysis, yields d-galactose and d-gluconic acid. So, the aldehyde group of the glucose unit is free. Lactobionic acid, on exhaustive methylation and hydrolysis, gives 2:3:4:6-tetramethyl galactose and 2:3:5:6-tetramethyl gluconic acid. Carbon-1 of galactose and carbon-4 of glucose form the glycosidic bond. Both α - and β -forms of lactose have been obtained. It has the following structure. Lactose has been synthesised in 1942.



LACTOSE

 β -d-Galactose α - or β -d-Glucose

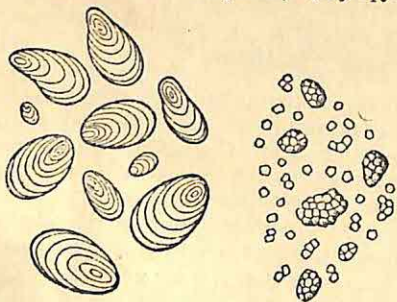
Uses.—Lactose is used in medicine, in making homœopathic and biochemic globules, and in silvering mirror. It is sometimes added to the milk diet of infants. Lactose is more slowly digested than maltose or sucrose. Undigested lactose in the large intestine exerts a laxative action, which, if in excess, may cause diarrhœa. The octa-nitrate is an explosive.

Relative sweetness of common sugars

Fructose	...	...	172	Maltose	...	...	32
Invert-sugar	...	...	130	Galactose	...	...	32
Sucrose	...	...	100	Lactose	...	...	16
Glucose	...	...	74	Saccharin	...	...	55,000

Polysaccharides such as starch, glycogen, dextrin, mucilages, cellulose, etc. are tasteless, apparently amorphous (many appear crystalline under X-ray) and mostly insoluble in water. Inulin and glycogen are soluble in warm water. On hydrolysis with warm, dilute mineral acids, or enzymes, they finally yield simple hexoses (very often glucose) or pentoses, but rarely both. Intermediate disaccharides may be formed, *e.g.*, maltose from starch and cellobiose from cellulose. Their molecular weights are not definitely known, but they are giant molecules, no doubt. They have the general formula $(C_6H_{10}O_5)_n$ except the pentosans, $(C_5H_8O_4)_n$, which occur in gums and woody tissues. Polysaccharides give acetates, ethers, etc. Their molecular structure is not completely known yet. It has, however, been established that they are mostly long, straight-chain molecules, the monosaccharides forming the links.

Starch or amylum, $(C_6H_{10}O_5)_n$, occurs in green plants, particularly in tubers, roots and seeds as a reserve food (*cf.* fats in animals). Starch grains from different sources have different shape and size (Fig. 45). Potato starch granules are the biggest, those of rice, the smallest. The main sources of starch are: potato—15-20%, maize—65-70%, rice—about 75% and wheat—60-70%. Tapioca, sago, arrowroot, sweet potatoes are also important commercial sources.



Potato starch

Fig. 45. Starch grains.

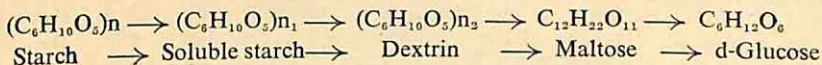
Rice starch

Manufacture of starch.—U.S.A. makes starch from maize (corn), Germany mainly from potato, U.K. and Japan from rice chiefly. It consists in removal of foreign matter from the cereal or plant. Potatoes are washed free from adhering dirt with water and rasped mechanically to a pulp, the cells are broken and starch grains exposed. The mass is thoroughly washed with water on a fine sifting machine which retains the coarser particles of cellulose but allows the smaller starch granules to pass through. The milky, aqueous suspension of starch and a little cellulose is allowed to stand; the starch settles at the bottom and lighter particles of cellulose, etc. are scraped off from the top. The mass is again treated with fresh water and allowed to settle; the supernatant liquid is decanted off. Starch is centrifuged to remove water and finally dried slowly in air or in ovens with gentle heat. The apparently dry product, however, contains 10-20% moisture, depending upon the relative humidity of the air. Starch from rice or maize is made similarly. Before washing with water, rice is treated with dilute caustic soda solution which removes, to some extent, gum and gluten and sets free the starch grains. Rice starch is more costly than potato starch (farina). The bye-products, cellulose and protein (gluten), serve as cattle food. Gluten is also added to special breads.

India imported 11,959 cwt. of starch, dextrin, etc. in 1955-56 valued at Rs. 3,27,715, mostly for the textile industries.

Properties.—Starch is a white, tasteless, odourless and amorphous solid, insoluble in cold water. It consists of two components, β -amylose or amylopectin which forms 80-90% and α -amylose 10-20% of starch. On boiling with water, α -amylose dissolves, the aqueous solution being dextro-rotatory. Amylopectin does not dissolve but forms a paste with water. Phosphoric acid (starch invariably contains a little phosphorus) occurs in amylopectin but not in amylose.

If starch is heated alone to about 200° , a gum-like product, *dextrin*, is formed. At higher temperature, various other products result. On heating under pressure with water, glycerine or with dilute acids, starch dissolves, but on cooling, a white substance (*soluble starch*) separates. This is believed to have a mol. wt. of about 33,000. On further hydrolysis, soluble starch forms dextrin, and finally, d-glucose:



Diastase quantitatively converts starch into maltose as does saliva or the pancreatic juice which contains *diastase*. Takadiastase (which contains *maltase*) hydrolyses starch to glucose and is given to patients to help digestion.

Starch does not reduce Fehling's solution or react with phenylhydrazine. α -Amylose gives a blue coloration with dilute iodine solution (in KI), which disappears on heating but reappears on cooling. An unstable compound is possibly formed between starch and iodine, or it is an adsorption phenomenon. This is a very delicate test also for iodine (as in iodometry). Amylopectin gives a violet colour with iodine. α -Amylose is believed to have a linear or unbranched structure of 100-700 glucose units, and amylopectin a highly branched one with 500-50,000 such units. While α -amylose quantitatively yields maltose with β -amylase, amylopectin gives only about 66% of theory.

Synthetic starch was made in 1940 by C. S. Hanes in vitro from glucose-1-phosphate with a phosphorylase present in potato and many plants. It closely resembles potato starch and has a mol. wt. 14,000-28,000. β -amylase converts it to maltose quantitatively.

Uses.—Huge quantities of starch are converted into glucose, alcohol, adhesives, etc., and also employed for sizing paper and finishing cotton fabrics. Its use in toilet preparations (dusting powder) and laundry is also important. Consumption of starch as food in the form of rice, bread, cornflour, oatmeal, potato, etc., is, however, the greatest. On cooking, starch is partly converted into dextrin. Starch acetate, a transparent gelatin-like mass, is used for making sweets; nitro-starch was used as a blasting explosive in the war of 1914-18 by U.S.A.

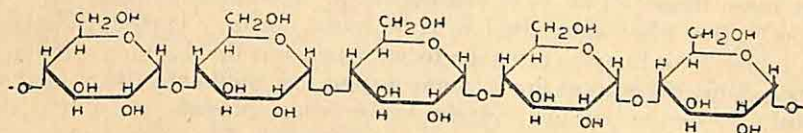
Dextrin or British gum, $(C_6H_{10}O_5)_n$, is manufactured by heating starch, moistened with a little dilute HCl and HNO_3 , to about 120° . It may also be obtained by the action of amylase on starch paste, or by simply heating starch to about 200° . It is a gummy, amorphous substance with a pale yellow colour, soluble in water. It has no reducing property. Boiling dilute acids give glucose. Dextrin is an adhesive (e.g., in postage stamps), a size for paper and also a vehicle for colour in textile printing. It gives blue, red or no coloration with iodine—depending upon the degree of hydrolysis.

Inulin, $(C_6H_{10}O_5)_n$, occurs in dahlia tubers, potatoes and Jerusalem artichokes (a kind of sunflower) and some lichens. On hydrolysis with dilute acids or *inulase*, it gives fructose almost quantitatively. Diastase, however, has no action on it. Inulin is a white powder, soluble in hot water, but practically insoluble in alcohol. It is laevo-rotatory, $[\alpha]_D = -40^\circ$, non-reducing and gives no coloration with iodine. Like starch, it is resistant to the action of alkalis. γ -Fructose units mainly constitute inulin, which during hydrolysis change to the more stable fructo-pyranose form (cf., cane-sugar, p. 285). Inulin contains some 30 fructose units per molecule. Glucose is a minor constituent of inulin.

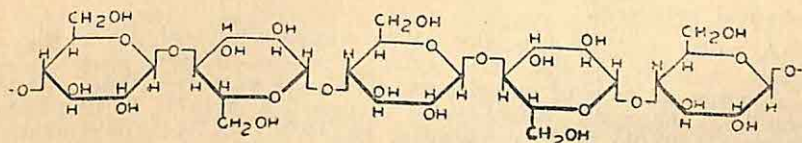
Glycogen, $(C_6H_{10}O_5)_n$, or *animal starch* occurs in the liver, muscle and white corpuscles of blood. It is also present in certain fungi and yeasts. Glycogen from plants and that from animals are strikingly similar. Dilute acids hydrolyse it to d-glucose. It is a reserved food in our system; the liver converts it readily into d-glucose to give energy in times of need. During muscular work, therefore, its concentration in the muscle diminishes. Glycogen may be obtained from the liver by boiling with 30% KOH which destroys liver tissues but not glycogen. It is a snow-white, amorphous, tasteless and odourless powder which gives a reddish-brown coloration with iodine. It forms a colloidal solution with water (and is insoluble in alcohol) which is dextro-rotatory, $[\alpha]_D = +198^\circ$. It does not reduce Fehling's solution, and resembles starch in many respects, e.g., its colour with iodine disappears on warming but reappears on cooling. Diastase converts glycogen to dextrin and maltose, acids produce only glucose. Glycogen closely resembles amylopectin structurally, being highly branched.

Cellulose, $(C_6H_{10}O_5)_n$, is by far the most abundant organic compound in nature. It has been calculated that the total weight of cellulose on earth is about 1,100 billion kilograms which is nearly half the weight of carbon dioxide in the atmosphere. Incidentally, carbon dioxide is the parent of this complex polysaccharide; plants build up cellulose from CO_2 and water. Cellulose forms the chief constituent of the cell walls of plants. Except in cotton, cellulose is almost invariably associated with lignin, the proportion of which varies widely. Purified cotton represents 99.6% cellulose. Other rich sources of cellulose are

wood, jute, flax, hemp, straw, etc. Celluloses from different sources are almost identical, being composed of glucose anhydride units, the number of which (*i.e.*, the degree of polymerisation) varies in different cases. They have high but variable molecular weights (from 20,000 to 20,000,00 depending upon the mode of preparation and the method of estimation). Both starch and cellulose yield, on hydrolysis, glucose finally. In starch the linkage is α -glucosidic while in cellulose, it is β -. Cellulose is a linear polymer but the major constituent of starch *viz.*, amylopectin, has branched chains. That is why cellulose solution can be obtained in the form of fibres (rayon) but not so starch. Acetyl-amylose gives elastic films but acetyl-amylopectin is brittle.



Starch.



Cellulose.

Preparation of pure cellulose.—Raw cotton is about 90% cellulose and 8% moisture; it contains traces of fatty, nitrogenous and mineral matters, pigment, etc. Cotton is first extracted with an alcohol-benzene mixture to remove fat and wax, and boiled with 1% NaOH solution with exclusion of air to free it from pectin matter and hemicelluloses. It is then treated with acetic acid to reduce the ash content, and finally bleached with dilute sodium hypochlorite. It is washed and dried; the dry mass contains 99.6% cellulose, called α - or normal cellulose.

From ligno-celluloses like wood, jute, etc., the normal cellulose may be obtained by removing the lignin from fat-free materials by treatment with chlorine, chlorine peroxide or sodium chlorite. Industrially, calcium sulphite, or caustic soda under pressure is generally employed for the removal of lignin. The resulting cellulose, obtained as a pulp, is utilised for making paper, etc. Quantitative filter paper is practically pure cellulose.

Properties.—Natural cellulosic fibres from different sources present different structures under the microscope. Cellulose decomposes on heating, and has no melting point. It is insoluble in, and heavier (sp. gr. 1.58) than, water. Cellulose is also insoluble in common solvents, but dissolves in cupric hydroxide in ammonia, called *Schweitzer's reagent*. From this solution, it is precipitated by alcohols, acids or salts. Cellulose has a complex structure and is little affected by ordinary chemicals including alkalis and cold, dilute acids. It however dissolves in conc. H_2SO_4 ; when the solution is diluted and boiled, it is quantitatively hydrolysed to glucose. The glucose may be fermented to alcohol.

Power alcohol is made from wood-waste, e.g., saw-dust, etc. Cellulose also dissolves in 42% HCl. With 15-20% caustic soda solution, under tension, the flat, ribbon-like fibres of cotton swell up and become almost cylindrical and assume a silky lustre. The process is called *mercerisation* after John Mercer who in 1844 observed this action of NaOH on cotton. Mercerised cotton is more durable and attractive, and more easily dyed than ordinary cotton.

With conc. H_2SO_4 and HNO_3 (1:3) at low temperature, cellulose gives mainly the ester, cellulose trinitrate (wrongly called nitro-cellulose) together with some dinitrate. *Gun-cotton* is a nitrocellulose containing more than 12.8% nitrogen, insoluble in nitroglycerine and soluble by not more than 15% in alcohol-ether (1:2). *Gun-cotton* ordinarily burns quietly, but when detonated in compressed form, it explodes violently. Cellulose is ordinarily resistant to enzymes, but the bacteria present in horse-dung decompose it, to some extent, to methane, CO_2 , etc. We cannot assimilate it but certain herbivorous animals can. The fact that we can digest starch (an α -glucoside) but not cellulose (a β -glucoside) indicates the importance of stereochemistry in some biological processes.

A paste of 37% *gun-cotton*, 58% nitroglycerine and 5% vaseline in acetone is called **cordite**, the smokeless powder. **Blasting gelatin** is made by absorbing 92 parts of nitroglycerine in 8 parts of nitrocellulose (containing about 12.3% nitrogen). Alfred Nobel discovered it in 1875. In 1955-56 India imported 12,207,085 lb. of it valued at Rs. 69,05,432. The lower nitrates of cellulose are also important. **Collodion** is a 3-5% solution of mainly the dinitrate in ether-alcohol mixture (3:1). When the solvent evaporates off, a strong, transparent film is left behind. It is extensively used in photography, in stopping bleeding, and as a leak-proof material. *Rexine*, an artificial leather, is made by coating a fabric with cellulose nitrate solution and a suitable pigment. The lower nitrates of cellulose are collectively called *pyroxylin*.

Celluloid or **xylonite** is made from lower nitrates of cellulose, chiefly di-nitrate, by heating it to about 75° under high pressure with camphor or its substitute as a plasticiser (about 20%) in alcoholic solution. It is a tough, transparent product, capable of being easily moulded while hot. It is not an explosive, though highly inflammable. It has an odour and is discoloured in light. It finds application in the preparation of numerous articles of daily use.

Cellulose has three free -OH groups per anhydro-glucose unit. So it can form mono-, di- and tri-esters. Like nitric acid, other acids such as acetic, sulphuric, etc., also produce corresponding esters of cellulose. When unsized paper (cellulose) is dipped into 80% H_2SO_4 for 15-20 seconds, it becomes more tough and less porous, probably being coated with cellulose disulphate. This is *parchment paper*. Cellulose acetates which cost more than the nitrates, are used for making artificial silk, dopes for aeroplane wings, paints and lacquers and specially, for non-inflammable moving picture film. In 1955-56 India imported 30.09 crores ft. raw cinema film valued at 2,22,16,631, she produces no raw film as yet though her film industry is now fairly big. *Carboxymethyl-cellulose*, made from soda cellulose and sodium chloroacetate, is a thickening agent, builder for synthetic detergents and size for textiles. The sodium salt is soluble in water. The commercial product has one $-\text{CH}_2\text{COOH}$ group per two glucose units.

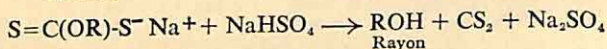
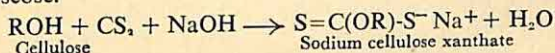
Paper.—The Chinese first made paper from the fibres of native trees. The main raw materials are wood, straw, bamboo, esparto grass, etc. The pulverised material, say bamboo, is digested with NaOH solution or calcium

bisulphite at 160°-170° for several hours under pressure (6-8 atmospheres). Lignin and some of the hemicelluloses are thus removed, and cellulose obtained as pulp. It is thoroughly washed and bleached with bleaching powder or sodium hypochlorite. The milky white, puffy mass of cellulose is beaten and run on to endless band of wire-gauze with sufficient water. The sheet of cellulose is then forced between steam-heated felt rollers, water is expelled and a sheet of blotting-paper-like material is obtained. This is sized with alum, rosin, gelatin, etc. to make it impervious to writing ink. We thus get writing paper. News print is cheap because 50% mechanical pulp containing lignin, etc., is mixed with the chemical pulp as prepared above. Blotting paper was discovered as a result of accidental omission of the size (rosin, alum, etc.) from some paper. By just touching the surface of the still moist paper with distinctive characters in the form of raised wires, water-mark is produced. The impression remains as a permanent thin place in the finished paper and allows more light to pass through it. China clay is added to produce a close sheet (art paper) for high grade printing.

India produced 2,53,008 tons of paper and board in 1958, which is insufficient to meet her demand. News print is now made here. A plant makes 20 tons of bleached pulp daily from bagasse. Annual paper consumption per capita in U.S.A. is about 350 lb., in Great Britain nearly 166 lb. but in India less than a pound due to appalling illiteracy.

Artificial silk or rayon.—Natural silk is a protein fibre secreted by insects, but artificial silk is made from cellulose. Count de Chardonnet first made artificial silk in 1884 from collodion. The production of rayon from cotton linters is simply a change in the mechanical structure of the carbohydrate fibre. This is done by forcing under pressure a solution of cellulose or its acetate through very fine orifices into a bath which removes the solvent and precipitates the cellulose in fine threads with a lustre. It is now done in two ways:

(i) *Viscose rayon.*—Purified wood pulp is treated with 18% NaOH at ordinary temperature. The resulting 'alkali cellulose' is combined with carbon disulphide to give cellulose xanthate, a yellow solid. This is dissolved in 3% NaOH, a highly viscous solution, called viscose, is obtained. Viscose after aging for 4-5 days is forced through fine jets into a bath of dilute H₂SO₄ or NaHSO₄, silky fibres of regenerated cellulose (or rayon) come out. From 1·12 tons of wood pulp 1 ton of rayon is obtained. Nearly 80% of the rayon is made from viscose.



(ii) *Acetate rayon.*—Cellulose triacetate is made by heating purified cotton linters with acetic anhydride and acetic acid with H₂SO₄ or ZnCl₂ as catalyst. The acetone solution of this ester is squeezed through fine orifices into a hot chamber when the solvent escapes, leaving behind lustrous fibres of rayon. The solvent is recovered (partly) and used again. Acetate silk is more costly but more durable and attractive. The finished product weighs about 1½ times the cellulose taken, and is not inflammable.

Rayon is about one-fourth as costly as natural silk, the cost of production being only about 30 times the price of wood pulp from which it is made. This explains the vast expansion of this industry in pre-war years, in which Japan excelled others. Natural silk may be easily distinguished from rayon by burning. The former gives an offensive odour of burnt hair, but not the latter. Rayon has a beautiful lustre and can take numerous shades with dye-stuffs; but ordinary rayon is less strong than real silk. The world production of rayon in 1957 was 5425 million pounds, but in 1891 it was only 30,000 lb. In

1925 rayon cost at Rs. 8-8 per lb. but in 1939 at only 9 annas (in Japan). In 1958 India produced 27,036 tons of viscose and 1812 tons of acetate rayon.

Cellophane or transparent paper is made by extruding viscose solution through a thin slot into an acid bath. The film thus obtained is a dust-proof wrapping material and an electric insulator. It is made water-proof by coating with a transparent nitrocellulose lacquer, and pliable by passing through glycerine solution.

Uses.—Cellulose is employed for making paper, artificial silk, gun-cotton, celluloid, lacquer varnish, cinema films, cordite, collodion, oxalic acid, textiles, power alcohol, etc. Cellulose acetate sheets are 'unbreakable glass' of commerce. Plastics are made from the acetate. Oxidised cellulose is used for surgical gauge and bandage; being acidic, it readily absorbs the alkaline fluid of the body.

Dextrans are highly branched glucosans made from sucrose solution and potassium phosphate by fermentation with *Leuconostoc mesenteroides* for about 24 hours. The bacteria or their enzymes utilise only the glucose component of sucrose. They have 1,6-glycosidic bonds between *d*-glucose units and a mol. wt. of over 10 lacs. A partially depolymerised product (mol. wt. 50,000-100,000), obtained by boiling a 5% solution of dextran with HCl for about 4 hours and precipitating with 45% alcohol, is used in medicine. Clinical dextran restores circulating blood volume, maintains blood pressure, and promotes survival in human shock. It has proved extremely useful as a blood plasma extender in the treatment of shock due to haemorrhage.

QUESTIONS

1. How is cane-sugar produced on a large scale? What are its physical and chemical properties? Outline a method for estimating the amount of cane-sugar in an aqueous solution.
B.Sc. Pass 1938, Dacca Uni.
2. Name three common foodstuffs which contain starch and explain how you would show starch to be present in them. How is glucose obtained from starch? In what ways does glucose differ from cane-sugar?
B.Sc. Pass 1938, Dacca Uni.
3. Write a short account of the carbohydrates giving their classification and properties, and mention the chief reactions used in determining the constitution of glucose.
B.Sc. Pass 1935, Dacca Uni.
4. Describe the classification of carbohydrates. What is the experimental evidence to show that glucose contains an aldehyde group and fructose a ketone group? How is glucose converted into fructose?
B.Sc. Pass 1939, Dacca Uni.
5. Describe the occurrence of glucose and fructose in nature and their more important reactions. How are they distinguished from one another? How is fructose obtained from glucose and vice versa?
B.Sc. Pass 1936, Allahabad Uni.
6. Indicate briefly the experimental basis on which the modern structure of glucose is assigned.
B.Sc. 1951, Calcutta Uni., B.Sc. 1937, Bombay Uni.
7. How is glucose obtained on a large scale? How will you obtain its osazone? Is this osazone the same as that of fructose?
B.A. Pass 1937, Bombay Uni.

8. How could you obtain glucose and fructose from cane-sugar? What is meant by the 'inversion of cane-sugar'? How is maltose obtained from starch?

9. What is artificial silk? How is it manufactured? Discuss the possibilities of rayon manufacture in India.

10. How are the following made; dextrin, celluloid, cordite, collodion?

11. Outline the present day views on the structures of glucose and fructose.
A. I. C. 1941; B.Sc. 1951, Gauhati Uni.

12. Describe briefly some industrial processes in which cellulose is the starting material.

13. Give an outline of the process of manufacture of sugar from sugar-cane.
B.Sc. 1936, Punjab Uni.

14. What are the principal disaccharides that you have studied? Mention the products formed when each of them is hydrolysed. Explain clearly why some of them possess reducing properties while other do not.

B.Sc. Degree Exam. 1942, Annamalai Uni.

15. Write an essay on the manufacture of paper.

B.Sc. 1941, Agra Uni. 1952, Rajasthan Uni.

16. By what chemical tests would you distinguish an aldohexose from a ketohexose? How may glucose be converted into fructose and vice versa?

B.Sc. Pass. 1942, Patna Uni.

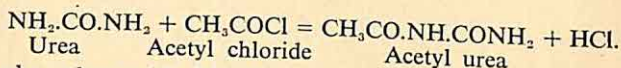
17. Outline the evidence for the pyranose structure of glucose.

B.Sc. Degree Exam. 1942, Andhra Uni., 1943, Benares Hindu Uni.

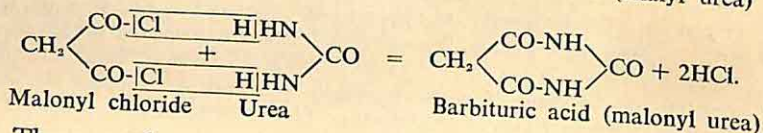
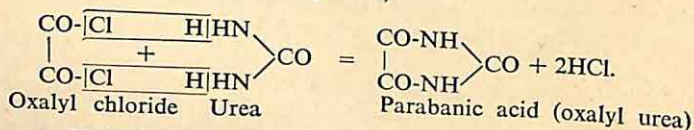
CHAPTER XXVIII

THE UREIDES

When a hydrogen atom of urea is replaced by an acyl group, we get a *ureide*. Acetyl chloride and urea give ureide of acetic acid or acetyl urea:

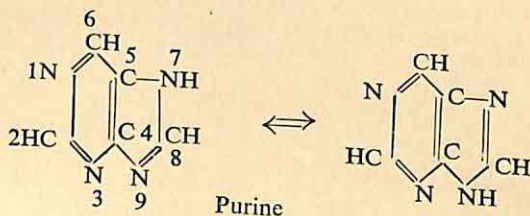


Similarly, other acid chlorides react with urea, and cyclic compounds may thus be formed, *e.g.*, oxalyl chloride yields parabanic acid, and malonyl chloride barbituric acid (p. 243).



These are heterocyclic as they contain nitrogen besides carbon in the ring. They are acidic, the H atoms of -NH- groups being replaceable by metals. The -NH- group (or -CH₂-) placed between two keto groups (as in barbituric acid), makes them highly reactive (*cf.*, succinimide, p. 245 and malonic ester, p. 242). The ureides are important for their use in medicine, *e.g.*, veronal (p. 267).

Purines, derived from two molecules of urea and one of a dibasic acid, are cyclic di-ureides. Purine, the mother-substance of the purine bases, does not occur in nature; Emil Fischer synthesised it. It exists in two tautomeric forms:



Purine is a colourless solid (m.p. 216°), highly soluble in water and amphoteric in character. The numerals in the above structure indicate the way its derivatives are named. Purines are of considerable physiological importance; they occur in our system as products of protein metabolism. Many are found in plants. The most important is uric acid.

Uric acid, C₅H₄O₃N₄, is 2:6:8-trihydroxypurine or 2:6:8-trioxy-purine; it occurs in the urine of the carnivora; human urine contains nearly 0.05% of its acid ammonium salt, an adult passing about 1 g.

per day. Scheele discovered the acid in urinary calculi (stones) in 1776. Its accumulation in the joints gives rise to gout and rheumatism; stones are formed in different parts of the system by its deposition. Normally, only traces of it occur in the blood, but in gouty patients the amount is considerably high. The excreta of birds and reptiles are rich in uric acid. White spots on the wings of the butterfly are due to this acid. The excrement of serpents contains 75% of almost pure ammonium urate, $C_5H_3N_4O_3(NH_4)$. Uric acid does not occur in plants. Monkeys excrete only traces of it. In the lower animals, uric acid is further oxidised to allantoin. Growth factors such as biotin and riboflavin, are cyclic ureides.

Preparation.—Excrement of snakes or birds (guano) is powdered and boiled with caustic soda solution until the evolution of ammonia ceases. The hot solution containing the sodium salt, is filtered and hydrochloric acid added to the filtrate. On cooling, crystals of uric acid separate. It is purified by dissolving in alkali and recrystallising from hydrochloric acid. It may be prepared by concentrating human urine and adding conc. HCl. Crystals of uric acid and urates have peculiar and characteristic shapes (Fig. 46). These are readily recognised under the microscope and helpful in urine analysis.

Properties.—Uric acid is a white, odourless crystalline powder, very sparingly soluble in water and insoluble in alcohol and ether. It dissolves in glycerol, strong H_2SO_4 , sodium acetate or carbonate solution. It decomposes, on heating above 250° , forming ammonia, urea, cyanuric acid, etc. It behaves as a weak dibasic acid; acetic acid liberates it from its salts. The acid salts are sparingly soluble in water, but the neutral salts are moderately soluble. With Na_2CO_3 , an acid salt and with NaOH, the neutral salt are obtained from uric acid. Lithium urate is fairly soluble in water. That is why lithium-water and alkaline mixtures were formerly prescribed for gouty patients. But uric acid or its monosodium salt does not combine with a soluble lithium salt to yield a soluble lithium urate. Urotropine in aqueous solution readily dissolves uric acid in the test-tube but not uric acid calculi in urine, owing probably to the low concentration that can be attained in urine.

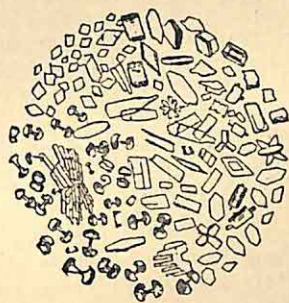
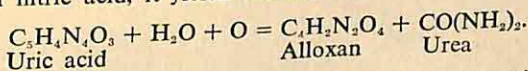
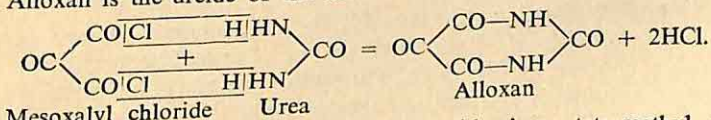


Fig. 46. Crystals of uric acid.

Constitution.—(i) From analytical data, uric acid is $C_5H_4N_4O_3$. (ii) On oxidation with nitric acid, it yields alloxan and urea.



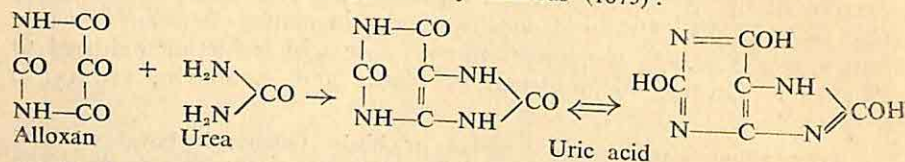
Alloxan is the ureide of the acid chloride of mesoxalic acid and urea:



(iii) On exhaustive methylation, the acid gives tetramethyl uric acid, $C_5(CH_3)_4N_4O_3$, the hydrogen atoms being replaced by methyl groups. On

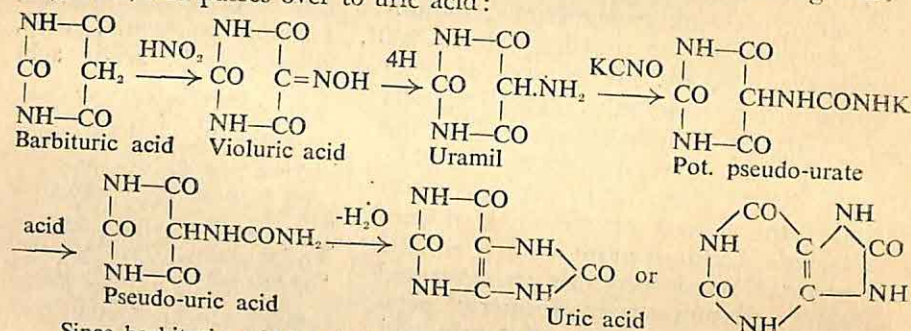
hydrolysis of tetramethyl uric acid with HCl, nitrogen is eliminated as methylamine but no NH_3 evolves, showing that the $-\text{CH}_3$ groups are directly linked to nitrogen. Hence, in uric acid, all the hydrogen must be attached to nitrogen. i.e., it has four $-\text{NH}-$ groups.

(iv) Of the four isomeric monomethyl uric acids, two, on oxidation, yield methylalloxan and urea and the other two, methylurea and alloxan. So the two urea residues are asymmetrically linked. These facts are explained by the following structure suggested by Medicus (1875):



In the equilibrium mixture, the ketonic form largely predominates. The hydrogen of the imido group in $-\text{CO.NH.CO}-$ (as in succinimide, p. 245) is salt-forming. This structure is supported by its synthesis, and its possible conversion into purine.

Synthesis of uric acid.—Barbituric acid is converted into its isonitroso derivative (violuric acid) with HNO_2 ; this, on reduction, yields aminobarbituric acid or uramil. Heated with potassium cyanate, potassium pseudo-urate is formed, which loses water, on boiling with 20% HCl, and passes over to uric acid:



Since barbituric acid is obtained from malonic ester by reacting with urea (p. 243), the above may as well be regarded as a synthesis from malonic acid.

Tests.—(1) *Murexide test*: Mix uric acid with a little conc. HNO_3 and evaporate the mixture to dryness on water-bath. Add a little dilute ammonia, an intense purple colour is produced due to the formation of ammonium purpurate or murexide. Add a drop of NaOH, the colour changes to blue. Caffeine also responds to this test.

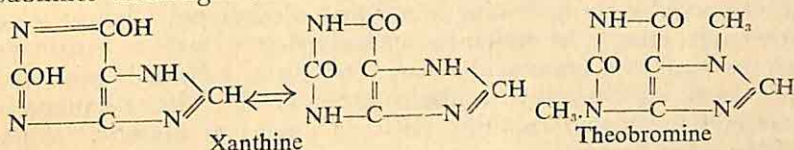
(2) It reduces Fehling's solution, decolorises acid or alkaline permanganate in the cold, and also chars on heating. Uric acid in strong H_2SO_4 solution can be estimated by titration with permanganate.

Uses.—4% ammonium urate ointment is used for eczema; the salt is given internally for cough. Murexide is an indicator for determining calcium ions.

Xanthine, 2:6-dihydroxypurine, $\text{C}_5\text{H}_4\text{O}_2\text{N}_4$, occurs in tea leaves, meat extract, malt, blood, liver and urine. Sprouting seedlings and beet-root also contain appreciable amounts. It may be obtained by reducing uric acid with sodium amalgam. Xanthine is an amorphous powder, very slightly soluble in water but readily soluble in alkalis. On

oxidation with KClO_3 in HCl , it yields alloxan and urea like uric acid. Xanthine forms salts both with acids and bases. It decomposes above 150° .

Theobromine, 3:7-dimethylxanthine, $\text{C}_7\text{H}_8\text{N}_4\text{O}_2$, occurs in cocoa beans (*Theobroma cacao*; *theos* god, *broma* food) to the extent of 1-2%, whence the name. It is a white, crystalline powder (m.p. 351°) with a faintly bitter taste, and slightly soluble in cold water. It sublimes unchanged at 290° and resembles caffeine.

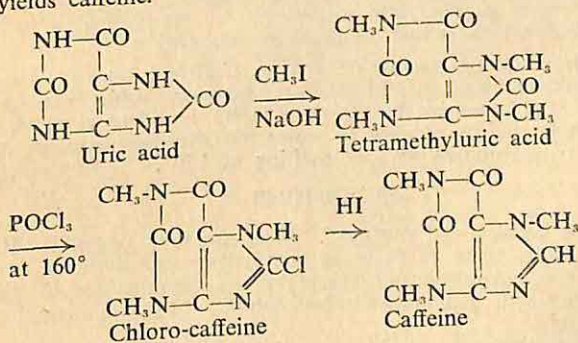


Theobromine is used in medicine as a diuretic, cardiac stimulant and in certain forms of dropsy. On methylation with dimethyl sulphate in NaOH solution, it gives 1:3:7-trimethylxanthine or caffeine. Caffeine is commercially made likewise. On oxidation, theobromine splits up into monomethyl alloxan and monomethyl urea.

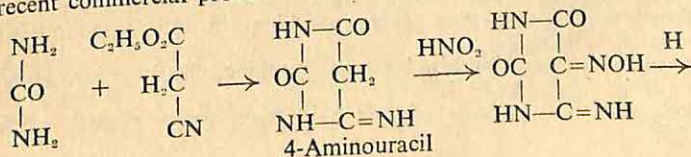
Caffeine, 1:3:7-trimethylxanthine, $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$, occurs in coffee beans (1-1.5%) (Latin *caffea* coffee), in tea leaves (2-4%), in kola nuts (1-2%), in cacao beans (0.1-0.8%) and in some other plants.

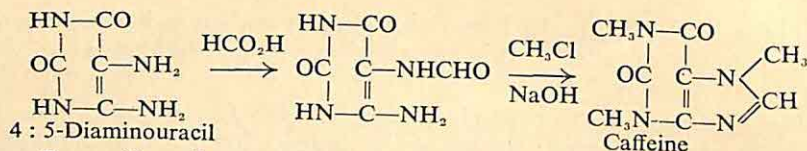
Preparation.—Caffeine is commercially extracted from damaged tea by boiling with four times its weight of water for about 20 minutes and filtered hot. The hot filtrate is treated with excess basic lead acetate which precipitates the albuminoids and tannins. The decanted liquor is treated with H_2SO_4 to remove the excess of lead. The acid solution is decolorised with animal charcoal and caffeine extracted with chloroform, after concentration. Chloroform is distilled off, and caffeine purified by crystallisation from water.

Synthesis.—Uric acid is exhaustively methylated to tetramethyluric acid which with POCl_3 at about 160° , forms chlorocaffeine. The latter, on reduction with HI , yields caffeine.



A recent commercial process starts from urea and cyanacetic ester :





Properties.—Long, silky, colourless needles of caffeine melt at 234° . Hydrated crystals (with 1 mol. of H_2O) are obtained from water and anhydrous crystals from organic solvents. Caffeine is fairly soluble in chloroform, boiling water and alcohol but slightly in cold water and ether. It sublimes unchanged and has a bitter taste. Caffeine is a weak monoacidic base, and forms salts only with strong acids such as citric, hydrochloric, etc. These salts stimulate the heart and the higher faculties. It is an important diuretic. We take caffeine when we drink tea or coffee; a cup of tea or coffee contains 0.1-0.2 g. of it. The effective dose of caffeine is 0.15 to 0.25 g.; about 80% of it is split up into urea in the body. With aspirin, caffeine citrate relieves pain. Caffeine gives the murexide test like uric acid (p. 298). India makes caffeine (about 20,000 lb. yearly) from tea waste.

Adenine, 6-aminopurine, $\text{C}_5\text{H}_5\text{N}_3$, occurs widely in the free state—in tea, sugar beet, yeast, urine, muscle, liver, etc. It is a constituent of nucleic acids which yield adenine on hydrolysis. It may be obtained from beet molasses or tea extract as well. Adenine is a crystalline solid (m.p. about 360° with decomposition), slightly soluble in water but readily soluble in mineral acids and alkalis, forming salts. It sublimes at 220° . HNO_3 converts the $-\text{NH}_2$ into an $-\text{OH}$ group and hypoxanthine is formed. Uric acid and PCl_5 react at 160° to give 2,6,8-trichloropurine which with ammonia forms 6-amino-2,8-dichloropurine. Hydriodic acid reduces the latter to adenine.

Guanine, 2-amino-6-hydroxypurine, $\text{C}_5\text{H}_5\text{N}_3\text{O}$, is also a constituent of nucleic acids (and nucleo-proteins). It occurs in guano (Peruvian *huanu*, dung), liver, animal tissues, and in many plants. Scales and skins of fish, reptiles, etc. contain large amounts of guanine. It may be obtained from guano by extraction with milk of lime, dissolving the residue in hot Na_2CO_3 and precipitating with acetic acid the guanine. It is an amorphous powder, almost insoluble in water and alcohol but dissolves in acids and alkalis, forming crystalline salts. Nitrous acid converts guanine into xanthine. In the animal system, guanine changes to xanthine which is then oxidised to uric acid.

Hypoxanthine, 6-hydroxypurine or sarkine, $\text{C}_5\text{H}_4\text{N}_4\text{O}$, occurs in both plants, e.g., tea and animals, e.g., in blood, liver, marrow, urine, etc. and also in nucleic acids. It is obtained by the action of HNO_3 on adenine, which establishes the structure. It is slightly soluble in water but dissolves in acids and alkalis, forming salts. It decomposes without melting at 150° .

QUESTIONS

1. What are ureides and purines? How are they related? How is uric acid obtained? State some of its main properties and reactions.
2. Discuss the constitution of uric acid and describe one of its syntheses. Show its relationship to caffeine and theobromine. B.Sc. (Principal Chemistry) 1941, Bombay Uni.
3. How does caffeine occur in nature? How is it manufactured? State some of its important properties and uses.
4. How would you pass from xanthine to theobromine, and from theobromine to caffeine?
5. Explain the relationship between xanthine, theobromine, caffeine and uric acid. B.Sc. London, 1931.
6. Describe the synthesis of uric acid from malonic acid. B.Sc. 1936. Punjab Uni.

CHAPTER XXIX

THE PROTEINS

The proteins are complex, nitrogenous substances of high mol. wts. They occur universally in varying amounts in the tissues of animals and cells of plants—no living cell is without protein (Greek *proteios*, primary). They are the main constituent of protoplasm. Animals contain much more protein than plants in which cellulose predominates. The dry material in animals, except mineral matter, fats and carbohydrates, consists mostly of proteins. Thus proteins represent about 15% of the average human body of which nearly 65% is water. They are essential food for animals who can live without fats and carbohydrates for a pretty long period but not without proteins. Plants build up their proteins from inorganic sources, but animals cannot. They depend upon plants for their protein supply; they build up animal proteins from the amino-acids of vegetable proteins as required. Unlike plants, animals rarely store proteins except in the form of living matter. Vegetable proteins undergo changes during assimilation by animals. We cannot assimilate all proteins. Proteolytic enzymes in the digestive tract hydrolyse the proteins of our food to amino-acids which are converted into new body proteins during growth, and also to hormones, bile salts, etc. Some are deaminated in the liver and kidneys; the NH_3 thus set free contributes to urea formation (about 80% of the protein-N passes out as urea) while the rest of the amino-acid molecule may form glucose or fatty acids, or is finally oxidised to CO_2 and water. To the 3,000 calories of heat required by an adult per day, only a little is contributed by proteins—their main functions are to provide for the growth of new tissues and repair of working parts. While 1 g. of fat, on combustion, gives 9.50 kcal. and 1 g. of carbohydrate 3.96 kcal., 1 g. of protein yields 4.40 kcal. In plants, proteins may occur as solid, or in solution in the cell sap. Reserve proteins of plants are commonly found in the solid form in seeds and vegetative organs of propagation. The protein content of some of our common foodstuffs is given below:

Source	Approx. protein %	Source	Approx. protein %
Cow's milk	... 3	Cooked fowl	... 24
Rice	... 8	Cooked beef	... 26
Cheese	... 33	Raw potato	... 2
Egg white	... 12.5	White bread	... 6.5
Pea	... 21	Banana	... 1.5
Egg yolk	... 16	Wheat	... 14
Maize	... 10	Groundnut	... 29

Composition.—Though proteins differ rather widely in their physical and chemical properties, their elementary composition is more or less the same. They contain carbon, hydrogen, oxygen, nitrogen and sulphur; some have phosphorus, iron, copper or iodine as well. Proteins contain some mineral matters, left as ash on ignition. It is not definitely known if these are constituent parts of protein mole-

cules; ash-free egg albumin is somewhat different from the ordinary. Their percentage composition is also fairly constant, considering the difficulties of obtaining them in the pure state. They usually contain C—50-55%, H—6.5-7.3%, O—19-24%, N—15-19%, S—0.3-2.4%.

The main building stones of protein molecules are α -amino-acids (p. 183) as glucose is of starch and cellulose. Proteins consist of chains of amino-acids united by peptide (amide) linkages, $-\text{CO}\cdot\text{NH}-$. They finally give amino-acids on hydrolysis. The type and number of amino-acids are different in different cases. For example, salmine from Rhine salmon consists of nearly 87% of *D*-arginine; hæmoglobin of blood contains 11% of histidine; silk fibroin is chiefly glycine, alanine and tyrosine. Some cereal proteins contain 40% of glutamic acid. Insulin, a crystalline protein, consists of 8 amino-acids—it has 30% of leucine, 21% of glutamic acid, 12% of cystine, 12% of tyrosine, 8% of histidine, etc. Emil Fischer, the pioneer worker in this field, showed during 1889-1918 that amino-acids in proteins are linked through amino and carboxyl groups.

Classification.—Based on physical and chemical characteristics, proteins are divided broadly into (A) **simple proteins** which give only α -amino-acids on hydrolysis. (B) **conjugated proteins** which contain, besides amino-acids, other ingredients such as phosphorus, carbohydrates, nucleic acids, etc. and (C) **derived proteins** which represent degradation products of natural proteins. The line of demarcation between these is not, however, always sharp.

A. **Simple proteins** are subdivided according to solubility. (i) **Protamines**, the simplest proteins, consist almost wholly of diamino-acids such as arginine, histidine, lysine, etc. Their mol. wts. are relatively low. They are soluble in water; their aqueous solution (which is strongly alkaline) does not coagulate on heating. Alcohol precipitates them from aqueous solution. They occur abundantly in fish, e.g., salmine (in the salmon), clupein (in the herring), etc. but not in plants.

(ii) **Histones** are readily soluble in water; they are precipitated from aqueous solution (which is strongly alkaline) by salts or ammonia. They are decomposed by protein ferments and are not coagulated by heat. Solutions of other proteins precipitate them. Globin of hæmoglobin and histones of the thymus gland are examples.

(iii) **Globulins** are insoluble in water but soluble in dilute solutions of neutral salts, dilute acids and alkalis. They are more easily salted out than albumins (e.g., on half saturation with ammonium sulphate or saturation with sodium chloride). They are slightly acidic; they are coagulated by heat like albumins. Globulins occur both in plants and animals—they are the common protein reserves of the higher plants. Globulins from plants have different solubility in salt solutions—they are coagulated by heat with great difficulty, and furthermore, they crystallise readily. Ovoglobulin of egg yolk, myosin of muscle, edestin of hemp seed are examples.

(iv) **Albumins** are neutral and soluble in water and dilute salt solutions. They are readily coagulated by heat. Once coagulated, they no more dissolve in water but are still soluble in acids and alkalis. If carefully isolated, they may be obtained in crystalline form. Saturated ammonium sulphate solution salts them out from their aqueous solution. Seeds contain only traces of albumin. Examples are ovalbumin from egg white, lactalbumin from milk, leucosin from wheat, ricin from castor oil seeds, etc.

(v) **Glutelins** resemble globulins in many respects. They are insoluble in neutral solvents (such as water, salt solutions, etc.) but readily soluble in dilute

acids and alkalis. They are of vegetable origin and represented by glutenin from wheat and maize, and oryzenin from rice.

(vi) **Gliadins or prolamines** are characterised by their solubility in 70-80% alcohol unlike others. They are insoluble in absolute alcohol, water or other neutral solvents. They are, however, soluble in acids and alkalis. They occur mostly in cereals. Examples are gliadin from wheat, zein from corn, hordein from barley, etc. Glutelins and gliadins are the chief constituents of gluten of grain seeds.

(vii) **Scleroproteins**, formerly called albuminoids, occur only in animals: they form their skeletal structure like cellulose in plants. They are insoluble in water, salt solution as well as dilute acids and alkalis. They are resistant to chemical or enzymic attack. To this group belong keratin of hair, horn, feather, nails, etc., collagen from hide, gelatin, silk fibroin, etc.

(viii) **Phosphoproteins** really belong to the conjugated proteins (as in American classification) but English classification includes these among simple proteins. As the name indicates, they contain phosphoric acid. They are insoluble in water but dissolve in alkalis and are precipitated by acids from their alkaline solution. Casein from milk, viteline from egg yolk are instances.

B. Conjugated proteins.—(i) **Chromoproteins** are coloured as the name suggests e.g., haemoglobin of blood which breaks up into globin (a protein) and a pyrrole derivative (haematin). They also occur in some pigmented animal fibres, e.g., black wool and hair. Visual purple of the eye is a chromoprotein. They usually contain metals such as iron, copper, magnesium, cobalt, etc.

(ii) **Nucleoproteins** constitute nuclei of cells and are compounds of nucleic acids and proteins such as histones and protamines. Viruses, responsible for infectious diseases, belong to this group, e.g., tobacco mosaic virus, a crystalline protein; they can multiply themselves in the living cell. They are weakly acidic and soluble in water, salt solutions and alkalis.

(iii) **Glycoproteins** contain a carbohydrate (e.g., glucosamine) and are acidic; they are soluble in alkalis. Mucin (of saliva) is an example. The jelly fish is very rich in glycoprotein.

C. Derived proteins result when natural proteins are subjected to the action of enzymes and other hydrolytic agents. Some of these have been synthesised. Derived proteins include:

- (i) **Proteans.**—Insoluble in water, formed by acids, water, enzymes, etc.
- (ii) **Meta-proteins.**—Produced by alkalies and prolonged action of acids; soluble in acids and alkalis but insoluble in water.
- (iii) **Coagulated proteins.**—Insoluble proteins formed by the action of heat, alcohol, etc.
- (iv) **Proteoses.**—Soluble in water, precipitated by $(\text{NH}_4)_2\text{SO}_4$ on saturation; not coagulated by heat.
- (v) **Peptones.**—Soluble in water but not precipitated by $(\text{NH}_4)_2\text{SO}_4$; not coagulated by heat; give biuret test.
- (vi) **Peptides.**—Soluble in water, neither precipitated by $(\text{NH}_4)_2\text{SO}_4$ nor coagulated by heat; give no biuret test usually. Many have been synthesised; they are condensation products of amino-acids.

Amino-acids occurring in proteins

I. Aliphatic amino-acids:

(A) Mono-amino mono-carboxylic acids

1. Glycine, $\text{CH}_2(\text{NH}_2)\text{COOH}$
2. Alanine, $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$
3. Valine, $(\text{CH}_3)_2\text{CHCH}(\text{NH}_2)\text{COOH}$
4. Leucine, $(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{NH}_2)\text{COOH}$

5. Isoleucine, $C_2H_5CH(CH_3)CH(NH_2)COOH$ 6. Serine, $CH_2OH.CH(NH_2)COOH$ 7. Threonine, $CH_3CH(OH)CH(NH_2)COOH$

(B) Sulphur-containing amino-acids

8. Cysteine, $HSCH_2CH(NH_2)COOH$ 9. Cystine, $HOOCCH(NH_2)CH_2S.SCH_2CH(NH_2)COOH$ 10. Methionine, $CH_3.S.CH_2.CH(NH_2)COOH$

(C) Mono-amino dicarboxylic acids (and their amides)

11. Aspartic acid, $HOOCCH_2CH(NH_2)COOH$ 12. Asparagine, $CONH_2.CH_2CH(NH_2)COOH$ 13. Glutamic acid, $HOOC.(CH_2)_2CH(NH_2)COOH$ 14. Glutamine, $CONH_2.(CH_2)_2CH(NH_2)COOH$

(D) Basic amino-acids

15. Lysine, $NH_2.CH_2(CH_2)_3.CH(NH_2)COOH$ 16. Hydroxylysine, $H_2N.CH_2.CHOH.(CH_2)_2.CH(NH_2)COOH$ 17. Arginine, $H_2N.C(=NH)NH.(CH_2)_3.CH(NH_2)COOH$ 18. Histidine (heterocyclic), $C_3N_2H_3.CH_2.CH(NH_2)COOH$

II. Aromatic amino-acids

19. Phenylalanine, $C_6H_5.CH_2CH(NH_2)COOH$ 20. Tyrosine, $HO.C_6H_4.CH_2CH(NH_2)COOH$ 21. Di-iodotyrosine, $HO.C_6H_2I_2.CH_2CH(NH_2)COOH$ 22. Thyroxine, $HO.C_6H_2I_2.O.C_6H_2I_2.CH_2CH(NH_2)COOH$

III. Heterocyclic amino-acids

23. Proline, $C_4NH_8.CO_2H$ 24. Hydroxyproline, $C_4NH_8O.CO_2H$ 25. Tryptophan, $C_8H_6N.CH_2CH(NH_2)COOH$

General properties.—The proteins except the chromoproteins are colourless—and barring a few *e.g.*, egg albumin, insulin, etc., they are hydrophilic colloids. They cannot, therefore, diffuse through parchment paper; by dialysis, proteins are generally freed from salts. They are insoluble in alcohol (gliadins however dissolve in 70-80% alcohol but not in absolute alcohol) and ether, most of them are insoluble in water (gelatin, egg albumin, etc. are soluble in water); with water some proteins form gels. Many, however, dissolve in salt solutions (*cf.*, solubility of amino-acids, p. 184)—physiological saline solution (0.8% NaCl) present in our system, keeps the protein matter in fluid form. They are optically active and are *lævo*-rotatory. Amino-acids having *d*-configuration are not assimilated by us. They have little food value. These occur in micro-organisms. The simpler members are tasteless and odourless. Proteins are non-volatile, they decompose on heating—and have no definite melting points. Some protein solutions coagulate on heating, the temperature of coagulation (usually between 55° and 75°) is determined by its specific nature, its pH value and the presence of electrolytes in it. Once coagulated, proteins seldom re-dissolve but may dissolve in acids and alkalis. Gelatine solution, an exception, sets to a gel on cooling. Alcohol, strong

electrolytes, and mineral acids coagulate some proteins. Many are 'salted out' from solutions by saturating them with ammonium sulphate. Proteins may be precipitated from colloidal solutions reversibly or irreversibly—boiling alone or with NaCl, acetic acid, etc., causes irreversible coagulation. Many dissolved proteins (e.g., in urine) are thus detected. Alcohol or acetone usually causes reversible precipitation.

Their molecular weights are very high—but not yet accurately known in many cases. From the iron content of hæmoglobin, its molecular weight has been found to lie between 16,000 and 17,000. That of casein (from its sulphur content) comes to 16,000. But the purity of the samples has not been conclusively shown. The mol. wt. of egg albumin by the osmotic pressure method (Sørensen) comes to about 43,000. By the ultra-centrifuge method (from the rates of sedimentation), Svedberg arrived at the same figure for the albumin of hen's egg. The other values by this method are 46,000 for insulin, 70,000 for horse serum, 310,000 for edestin, 8,910,000 for hæmocyanin, 10,600,000 for tomato virus and 40,000,000 for tobacco mosaic virus. Light scattering method gives the figure for egg albumin as 45,700, for horse serum, 76,600, for edestin, 335,000, for hæmocyanin, 6,340,000 and for tomato virus, 9,000,000. These may represent the size of the micelle (formed from several molecules).

Some of their physical properties may change without there being any change in their elementary composition. This may occur when they remain in contact with water or alcohol for a long time, and more particularly, when they are heated or treated with acids, alkalis or ultra-violet light, or even on shaking. Their solubilities in water or salt solutions thus decrease. They may lose physiological activity or capacity to crystallise; their mol. wts. may also be affected. This is known as *denaturing*. Many proteins give amines (with loss of CO_2) when heated cautiously, especially in indifferent, high-boiling solvents. Leucine thus gives iso-amylamine. The action of bacteria is more or less similar; proteins thus undergo putrefaction.

Some proteins are visibly fibrous but not visibly crystalline, e.g., silk, hair, etc. Others are visibly crystalline but not visibly fibrous, e.g., egg albumin, insulin, etc. These are called fibrous and corpuscular proteins respectively. But casein, a non-fibrous protein, has been obtained in the fibrous form. *lanital*, an artificial wool discovered in Italy and made on a commercial scale, is essentially casein (a solution of casein in NaOH and carbon disulphide is forced through fine orifices into a sulphuric acid bath, just as rayon is made, to obtain the fibre which is then hardened by treatment with formaldehyde. The X-ray diffraction patterns of the fibrous proteins reveal their crystalline structure. 'Denatured' corpuscular proteins also give similar X-ray photographs, indicating a bundle of stretched polypeptide chains. They can, therefore, be made into artificial fibres. *Nylon*, a purely synthetic polyamide fibre, made from adipic acid and hexamethylenediamine, is an excellent substitute for natural silk. It has a structure similar to that of synthetic polypeptides of Emil Fischer, e.g., $[-\text{CO}-(\text{CH}_2)_4-\text{CO}-\text{NH}-(\text{CH}_2)_6-\text{NH}-]_x$.

Like amino-acids, proteins are mostly amphoteric in their behaviour, the acidic or basic tendencies being determined by the relative number of free $-\text{COOH}$ or $-\text{NH}_2$ groups. In acidic solution, they generally behave as bases and in basic solutions, as acids. The behaviour of a protein is thus largely influ-

enced by the pH (i.e., the hydrogen-ion concentration) of the solution. The particular pH at which the number of anions and that of cations are equal, is known as its *iso-electric point*; the positive charges on the zwitter-ion (p. 184) exactly balance its negative charges. It is not, however, pH 7 (it is generally on the acid side) and varies with different proteins. Thus for casein, it is 4.6; for hæmoglobin, 6.8, for glutenin, 4.4, for insulin, 5.3, for protamine, 12.2 and for egg albumin, 4.8. A protein in colloidal solution is most easily coagulated on account of its electrically neutral character at the iso-electric point; swelling, solubility or viscosity is the minimum.

Vegetable proteins are not fundamentally different from animal proteins (cf., animal and vegetable fats); for example, it is not possible to establish the identity of any particular albumin or globulin. Vegetable proteins, however, yield comparatively more glutamic acid and ammonia than do animal proteins. Some proteins e.g., prolamines, occur only in the vegetable world. From a study of the crystalline enzymes such as *urease*, it appears that enzymes are proteins. Insulin (the deficiency of which causes diabetes) and some other hormones are proteins; the viruses (sub-microscopic agents passing through a filter that retains living cells) that cause disease, are nucleoproteins.

Reactions of proteins.—(i) *Biuret reaction*: On adding a few drops of a very dilute solution of CuSO_4 to a solution of protein made alkaline with an excess of NaOH solution, a violet colour is developed. This is due to the presence of at least two $-\text{NH}-\text{CO}-$ groups in proteins as in biuret (p. 266). All proteins and many of their decomposition products but not free amino-acids respond to this test.

(ii) *Millon's reaction*.—With a few drops of Millon's reagent (an aqueous solution of mercuric and mercurous nitrate having a trace of free HNO_2), proteins that contain tyrosine (an amino-acid with a phenolic radical) give brick-red coloration or ppt. on boiling. The colour is specific for the phenol group; gelatin, for example, does not give this test.

(iii) *Xanthoproteic reaction*.—A protein solution, on warming with a little conc. HNO_3 , turns yellow (Greek *xanthos*, yellow; on making it alkaline with ammonia, the colour changes to orange. It is a delicate test for proteins with aromatic nuclei. The yellow stain conc. HNO_3 produces on the skin, is due to this reaction.

(iv) *Molisch's reaction*.—To a protein solution taken in a test-tube, is added an alcoholic solution of α -naphthol, and then conc. H_2SO_4 is cautiously poured down the side of the test-tube. A violet colour is formed at the junction of the two liquids. Only proteins containing a carbohydrate respond to this test. The colour is probably due to the formation of furfural from the carbohydrate, which reacts with α -naphthol.

(v) *Lead sulphide test*.—On boiling a protein solution with NaOH and lead acetate, a black ppt. of lead sulphide appears. Proteins having sulphur as $-\text{S}-\text{S}-$ or $-\text{SH}$ (e.g., in cystine or cysteine) give this test.

(vi) *Coagulation test*.—A protein solution, acidified with acetic acid, coagulates on heating if it contains albumin. The test is not delicate as traces of protein cannot thus be detected.

(vii) *Ninhydrin reaction*.— α -Amino-acids, proteins or their decomposition products, having a free $-\text{COOH}$ and an α -amino group, produce a blue colour on heating with triketohydrindene hydrate (ninhydrin). This is widely used in detecting amino-acids by paper chromatography. But ammonium salts and some amines also give this test.

Isolation of proteins.—In many cases, proteins may be obtained in more or less pure form by mechanically separating the accompanying matter. For instance, starch of wheat flour can be removed by washing and separated from

any, is removed. The solid that has been extracted contains the diamino-acids, dicarboxylic acids, etc. The individual acids from each fraction are then separated by precipitation, fractional crystallisation, paper chromatography, etc. In *Brazier-Schryver method*, the different solubilities of the copper salts of amino-acids are utilised for their separation.

Estimation of proteins is done by carrying out the preparation quantitatively. The method most extensively followed in food chemistry laboratories is to estimate the nitrogen by Kjeldahl's method, and calculate the proteins in a sample by multiplying the percentage figure for nitrogen by a factor (usually 6.25). This, however, does not always give accurate results because unlike animal proteins (which generally contain very close to 16% of nitrogen) many vegetable proteins contain more nitrogen (18% or higher).

Emil Fischer tried to build up the protein molecule by combining amino-acids. He (1907) prepared a polypeptide, $C_{48}H_{80}O_{16}N_{18}$, from 18 amino-acid mols. with a mol. wt. of 1213 (so, far less complex than the protein molecule whose mol. wt. is probably a multiple of 34,000), and the high-sounding name, 'l-leucyl-triglycyl-l-leucyl-triglycyl-l-leucyl-octo-glycyl-glycine.' It is practically the nearest approach to the natural proteins, and the most complex of the synthetic polypeptides—it has 816 isomerides. Abderhalden, a pupil of Emil Fischer, has later on obtained a polypeptide consisting of 19 amino-acids. Synthetic polypeptides give biuret reaction like proteins.

Some micro-organisms grow so rapidly in suitable media that they are utilised as sources of protein. A variety of yeast was used in Germany during the war of 1914-18 to synthesise (by rapid growth) protein food from beet-molasses which is rich in nitrogenous compounds. The dried yeast contains half its weight of protein and was a valuable cattle-food. 'Marmite' is an extract of such material.

Baker's yeast (which is mostly protein) can be treated to give products resembling meat in appearance and flavour. It possesses a high nutritive value and was, during the second world war, recommended as a substitute for animal protein in human diet. Compressed yeast can be economically grown on a large scale with ammonium salts (ammonia made by Haber's process from air) as the source of nitrogen and molasses as the source of carbon. The nitrogen of the air is thus converted into protein—undoubtedly a big achievement.

Gelatine forms an insoluble compound with tannin; this is commercially utilised in the tanning of hide into leather. **Casein** from milk is used in making invalid foods, in the manufacture of plastics with formaldehyde (used in making buttons), sizing of paper, in making casein glue, etc. Soya bean protein is made into a fibre. Albumin tannate is used as an intestinal astringent; peptonised iron made from pentone and iron oxide, is a nutrient; mercuriol, containing 20% mercury combined with nucleic acid, is a local antiseptic.

Plasma protein in aqueous solution, obtained from blood after removing blood cells by centrifuging, is now widely used for treating shock due to major operations or serious injuries.

QUESTIONS

1. What are proteins? By what specific reactions are they detected?
2. What are the building stones of protein molecules? State some of the important properties of the proteins.
3. Discuss the results obtained by the hydrolysis of the proteins. (B.Sc. London, 1932).
4. Explain: iso-electric point, zwitter-ion, amphoteric compounds and polypeptides.
5. Mention, with examples, the groups into which proteins have been classified.

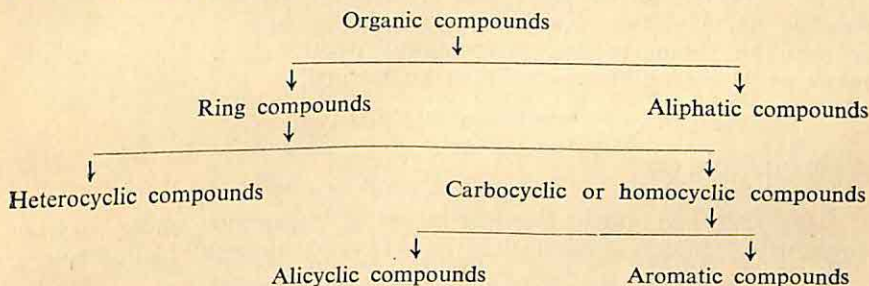
CHAPTER XXX

THE CYCLOPARAFFINS

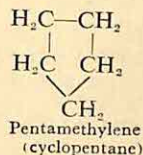
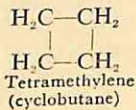
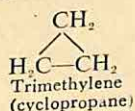
We have so far discussed the aliphatic compounds, *i.e.*, open-chain hydrocarbons and their derivatives which include some closed-chain compounds such as lactones, anhydrides and imides of dibasic acids, ethylene oxide, etc. There are quite a large number of compounds having three, four, five or, more commonly, six atoms of carbon in rings of great stability. They differ in some respects from the aliphatic, and are called **cyclic compounds**. These comprise of:

(i) **Carbocyclic or homocyclic compounds** having only carbon in the ring; *e.g.*, benzene, C_6H_6 . They are either (a) *Alicyclic (aliphatic cyclic) compounds* such as cyclopentane, C_5H_{10} (p. 63), cyclohexene, C_6H_{10} , etc. or, (b) *Aromatic compounds* such as benzene, naphthalene, etc.

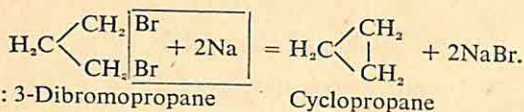
and (ii) **Heterocyclic compounds** with one or more elements other than carbon in the ring, *e.g.*, pyridine, C_5H_5N .



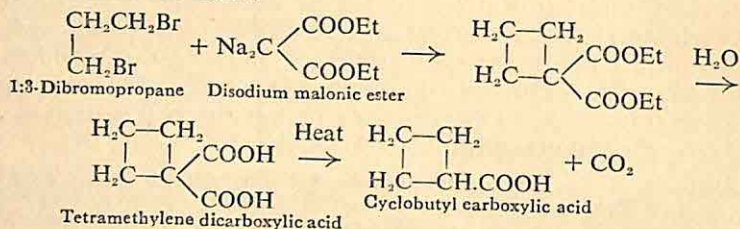
Polymethylenes, cycloparaffins or cycloalkanes are alicyclic hydrocarbons having the general formula, C_nH_{2n} . They are isomeric with the olefines (p. 63), but *saturated* and quite stable. They occupy an intermediate position between aliphatic and aromatic hydrocarbons. Polymethylenes are also called *naphthenes* as some of them, *e.g.*, cyclopentane and cyclohexane, occur in the naphtha fraction of petroleum. Sterols, bile acids, sex hormones, vitamin D_2 (calciferol), etc., contain alicyclic rings. Alicyclic compounds occur widely in plants as essential oils (*e.g.*, terpenes) and as naphthenes in Russian petroleum. Cycloparaffins are named according to the number of methylene groups in the molecules:



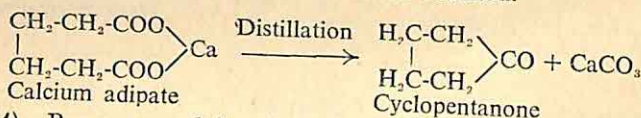
Preparation of polymethylenes and their derivatives.—(1) Cycloparaffins may be prepared by treating α, ω -dibromoparaffins (*i.e.*, having terminal bromine atoms) with sodium (*internal Wurtz reaction*). The lower members up to cyclohexane can thus be made; if the halogens are further apart than 1:6 positions, paraffins are obtained by Wurtz reaction.



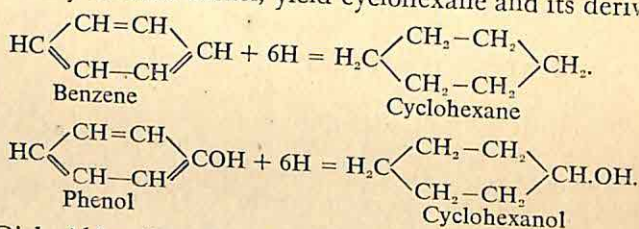
(2) Alicyclic acids result on treating α, ω -dibromoparaffins with disodio-malonic ester:



(3) Calcium salts of higher dibasic acids (of the oxalic acid series), on dry distillation, yield alicyclic ketones. Three-membered rings cannot, however, be obtained thus. They are termed by the corresponding name of the cycloparaffin ending with 'one'. Hydriodic acid reduces the ketone to the corresponding hydrocarbon. Rings with as many as 34 carbon atoms can thus be formed.



(4) Benzene and its derivatives, on hydrogenation under pressure in presence of finely divided nickel, yield cyclohexane and its derivatives.

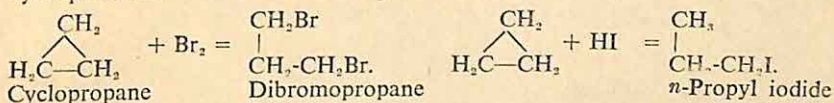


(5) By Diels-Alder Reaction (p. 251) various alicyclic compounds may be prepared.

Properties of polymethylenes.—The cycloparaffins, except the first two members which are gases, are colourless liquids or solids. Their density increases with molecular weight. They usually boil at higher temperatures than isomeric olefines or corresponding paraffins as shown below. This is true about their derivatives as well.

No. of C-atoms in the mol.	C_nH_{2n} (cyclic)	C_nH_{2n} (olefine)	$\text{C}_n\text{H}_{2n+2}$ (paraffin)
	Density	b.p. °C	b.p. °C
3	gas	-34	-44.5
4	0.7038	13	0.6
5	0.7635	49	36.3
6	0.7934	81	69
7	0.8252	118	98.4
8	0.8502	149	126
		120.5	

Polymethylenes with five or more carbon atoms are quite stable. They behave generally like aliphatic hydrocarbons. For example, bromine gives substitution products with cyclobutane and higher homologues. But with cyclopropane, dibromopropane is obtained. Cold pot. permanganate solution has no action on cycloparaffins as on paraffins (but *cf.*, ethylenes, p. 59). The cyclopropane and cyclobutane rings are comparatively less stable. Cyclopropane, for example, gives an open-chain compound with bromine in sunlight, or hydriodic acid. Hot hydriodic acid and cyclobutane give *n*-butyl iodide; other higher cycloparaffins are unaffected by the acid.



Cyclopropane yields propylene when passed through a red-hot tube. By hydrogenation in presence of nickel, cyclopropane forms propane at 80°, and cyclobutane gives *n*-butane at about 120°, cyclopentane forms *n*-pentane at 300°. Higher members remain unaffected by such treatment. Baeyer tried to explain such instability by his *strain theory* (1885).

Relative stability of ring compounds.—According to van't Hoff and Le Bel (p. 193), the angle between any two valency bonds of carbon, directed in space, is 109°28'. In saturated aliphatic compounds, it is possible to conceive all the carbon atoms in one plane, without distortion of valency bonds. In compounds with a double or triple bond (pp. 60, 66), the bonds are 'deflected' from their normal directions, thereby causing a 'strain' in the molecule. In trimethylene, the carbon atoms lie at the corners of an equilateral triangle, and hence the angle between them is 60° if it is assumed, as Baeyer did, that the C atoms in cyclic compounds also lie in the same plane. So the valencies engaged, in carbon-carbon linkage have suffered a distortion of $\frac{1}{2}[109^\circ 28' - 60^\circ]$ or 24°44'. Similarly for cyclobutane (a 4-membered ring) it is $\frac{1}{2}[109^\circ 28' - 90^\circ]$ or 9°44'. Calculated in the same way, the magnitudes of deflection of the valency bonds from the normal in the polymethylenes are:

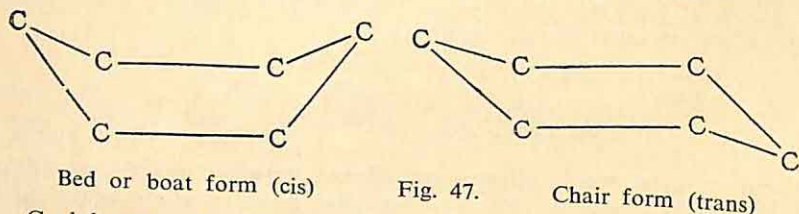
Cyclopropane	+24°44'	Cyclohexane	-5°16'
Cyclobutane	+ 9°44'	Cycloheptane	-9°33'
Cyclopentane	+ 0°44'	Cyclo-octane	-12°46'

+ Sign indicates inward and - sign outward displacement.

According to Baeyer, the strain is a rough measure of the instability of these rings. The strain is the greatest in cyclopropane, and the least in cyclopentane. Their behaviour supports this view. The former behaves more or less like an olefine and the ring is easily ruptured, while the latter is stable like a paraffin. Molecular refraction, molecular dispersion, heat of combustion, parachor values, etc., of alicyclic compounds are in favour of Baeyer.

This simple explanation of the stability of cyclic compounds is not, however, wholly satisfactory inasmuch as six-membered rings occur in much greater abundance than five-membered ones, though the strain

in the latter is apparently the least. Then again, cycloparaffins from cycloheptane upwards should be more and more unstable, which is also not true. In fact, Ruzicka has synthesised rings containing as many as 34 carbon atoms by distilling in vacuo at 300° thorium or cerium salts of dibasic acids with copper powder; these are remarkably stable. This is because all the carbon atoms do not lie in the *same* plane, and the rings are buckled so as to produce practically *no* strain. Sachse (1890) first suggested such strainless models for cyclohexane:



Cyclohexane should, therefore, exist in two stereo-isomeric forms. But actually, only one is known. According to Mohr who elaborated Sachse's idea, these configurations continuously change from one into the other—the ring system being dynamic.

Cyclopropane or trimethylene, C_3H_6 , is a colourless and pleasant-smelling gas obtained by treating 1:3-dibromopropane in boiling xylene solution with sodium. In daylight, it gives a mono-substitution product with chlorine, but bromine or hydriodic acid opens up the ring, giving 1:3-dibromopropane and *n*-propyl iodide respectively. Passed through a red-hot iron tube, it forms propylene, and on catalytic hydrogenation, it gives propane. Its corresponding ketone or alcohol is unknown. Propane (from cracked petroleum) is commercially chlorinated to 1:3-dichloropropane which forms cyclopropane in 80% yield with zinc dust. It is a safe but costly anæsthetic, producing unconsciousness. But the disadvantage is that a mixture of cyclopropane (25-70% by volume) with oxygen is explosive and a spark of static electricity may start the explosion. Cyclopropane can be readily distinguished from isomeric propylene which decolorises dilute alkaline permanganate solution in the cold, but cyclopropane does not. It has a characteristic odour and pungent taste. It is slightly soluble in water but freely soluble in alcohol.

Cyclobutane or tetramethylene, C_4H_8 , is also a pleasant-smelling gas, unaffected by bromine, $KMnO_4$ or HI in the cold. On catalytic hydrogenation with nickel at 120° , *n*-butane is obtained. It is usually prepared by the hydrogenation of cyclobutene at 100° with nickel. 1:4-dihalogen derivatives of *n*-butane do not, however, yield cyclobutane by ring closure. Cyclobutanol (b.p. 123°) is quite stable, resembling *n*-butanol.

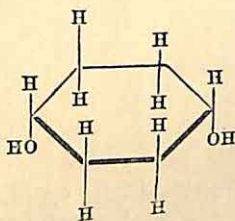
Cyclopentane or pentamethylene, C_5H_{10} , occurs in naphthenic petroleum, and can be obtained from 1:5-dibromopentane, $CH_2Br(CH_2)_3CH_2Br$, and zinc. It is a mobile liquid (b.p. 49°), remarkably stable; bromine cannot open the ring. The halogens, in

presence of light, produce substitution derivatives—chloro- bromo-cyclopentanes, etc. It gives *n*-pentane by catalytic reduction over platinum at 300°. It is thus much more stable than cyclobutane. It may be nitrated with concentrated HNO_3 in the cold or dilute HNO_3 at 100°. Cyclopentanone (p. 310) may be reduced to cyclopentane with zinc-mercury couple and HCl .

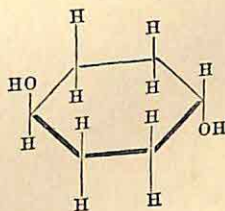
Naphthenic acids are monocarboxylic, derived from alkylated cyclopentane; they occur in small amounts in Russian petroleum. Their copper salts are very good antiseptics, lead, cobalt and manganous salts are oxidation catalysts (driers) for paints. Chaulmoogric acid (m.p. 68°), present in chaulmoogra oil (a remedy for leprosy), is a cyclopentene derivative.

Cyclohexane or hexamethylene, C_6H_{12} , occurs in various petroleum. Essential oils of plants *e.g.*, terpenes, are rich in cyclohexane derivatives. Methylcyclopentane gives cyclohexane on heating above 450° with chromic oxide. It is manufactured by hydrogenation of benzene in presence of nickel at about 200°. Cyclohexane is a colourless, fragrant liquid (b.p. 81°), resembling the paraffins closely. Chlorine and bromine produce substitution products, and hot conc. HNO_3 oxidises it to adipic acid, $\text{HOOC}(\text{CH}_2)_4\text{COOH}$. For making nylon, adipic acid is obtained by oxidising cyclohexane with air in presence of cobalt salt at about 120°. Fuming H_2SO_4 converts it to benzenesulphonic acid, $\text{C}_6\text{H}_5\text{SO}_3\text{H}$. Cyclohexane is a commercial solvent. Gammexane, the well-known insectide, is hexachlorocyclohexane (p. 320).

The six substituents in benzene and its derivatives lie in the plane of the ring but in cyclohexane, they occur in two planes (parallel to that of the ring). Consequently, when two H-atoms linked to two different C-atoms are replaced, a special type of spatial isomerism results. Two compounds are thus possible according as the substituents lie in the same plane (cis-form) or in different planes (trans-form). Quinitol (1:4-dihydroxy-cyclohexane) occurs in two stereoisomeric forms (both optically inactive). This is similar to the isomerism of maleic and fumaric acids (p. 249), the ring prevents free rotation of carbon atoms like the double bond.



Cis-quinitol (m.p. 102°)



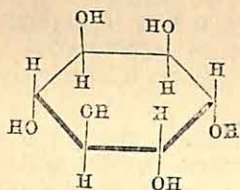
Trans-quinitol (m.p. 139°)

Cyclohexanol or hexaline, $\text{C}_6\text{H}_{11}\text{OH}$, the corresponding alcohol, is a colourless liquid (b.p. 160°), with a smell of camphor. It is a solvent for cellulose esters and phenolic resins; it improves the cleansing power of soap. It is made by the hydrogenation (under 4 atmospheres pressure) of phenol in presence of nickel at 160-170°. Chromic acid oxidises cyclohexanol to cyclohexanone, $\text{C}_6\text{H}_{10}\text{O}$, a ketone, which is also formed if phenol is hydrogenated well above 200°. On oxidation

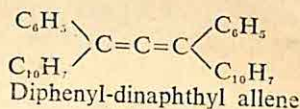
with conc. nitric acid or alkaline pot. permanganate, it gives adipic acid (p. 246), used in making Nylon.

Partially or fully hydrogenated benzene and its derivatives are called *hydroaromatic compounds*; they possess olefinic or paraffinoid properties rather than aromatic. Cyclohexane, cyclohexanol and cyclic terpenes are examples.

Cyclohexanehexol or inositol, $C_6H_6(OH)_6$, which is isomeric with glucose, is obtained by reducing hexahydroxybenzene, $C_6(OH)_6$, in presence of platinum black. It is sweet and occurs in the liver, heart and brain, and as *phytin*, the hexaphosphoric ester, $C_6H_6(OPO_3H_2)_6$, in plant cells. It exists in 8 isomeric (cis-trans) forms of which only one has an asymmetric structure, and is optically active. The d-form occurs in pine trees. The optical activity of inositol is specially interesting inasmuch as it *contains no asymmetric carbon atom* (see p. 194) but the molecule itself has asymmetric structure (it cannot be superimposed upon its mirror image). The benzene ring, like a double bond, restricts free rotation of atoms or groups and makes these stereoisomers possible. Like inositol, certain derivatives of diphenyl and of allene, $H_2C=C=CH_2$, also exhibit optical activity.



Inositol (d- or l-)



Cycloparaffins, C_nH_{2n} .

Name	Formula	m.p. °C	b.p. °C	sp. gr. 20°/4°
Cyclopropane	$(CH_2)_3$	-126.6	-34	.688 at -40°
Cyclobutane	$(CH_2)_4$	-50	13	.704 at 0°
Cyclopentane	$(CH_2)_5$	-94	49	.746
Cyclohexane	$(CH_2)_6$	6.5	81	.778
Cycloheptane	$(CH_2)_7$	-12	118	.810
Cyclo-octane	$(CH_2)_8$	14.4	149	.839

QUESTIONS

1. State briefly Baeyer's strain theory as applied to cyclic compounds, and describe the lines on which the theory has been extended and developed. (B.Sc. London, 1931).

2. How are cyclohexane and cyclohexanol manufactured? What are their uses? How could you distinguish cyclohexane from normal hexane?

3. Describe different methods by which cycloparaffins have been synthesised. (B.Sc. Hons., 1937, Dacca Uni.).

4. What do you know about the polymethylenes? What is Baeyer's strain theory? (B.Sc. Hons. 1933, Dacca Uni.).

5. What are the various methods available for the synthesis of polymethylenes? (B.Sc. Degree Exam. 1941, Annamalai Uni.).

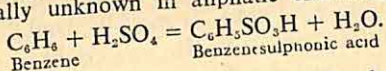
CHAPTER XXXI

THE AROMATIC HYDROCARBONS

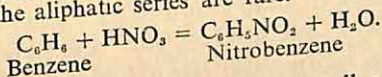
The earlier chemists classified substances mainly according to their physical properties—thus all gases were commonly called 'air'; 'oil' of vitriol, 'milk' of lime, 'butter' of antimony, etc., are familiar examples. Plant products such as oil of bitter almonds, gum benzoin, oil of lemon, balsam of Tolu, oil of wintergreen, etc., named likewise, did not quite fit into the established classes of compounds then known; they were designated as *aromatic* on account of their pleasant 'aroma' or smell. With the development of organic chemistry, it was discovered that these were cyclic compounds, and could be regarded as derivatives of a mother substance, benzene, C_6H_6 , as aliphatic compounds may be considered to have been derived from methane. Compounds derived from, or related to, benzene are called *aromatic compounds* though most of them are devoid of aroma, and some have a nauseous odour. Their properties are somewhat different from those of the aliphatic. They, like the aliphatic, consist of hydrocarbons, alcohols, aldehydes, acids, etc. All organic compounds cannot, however, be grouped into these two water-tight compartments, aliphatic and aromatic; there are others that occupy intermediate positions and possess a blend of the properties of both (e.g., the alicyclic compounds).

Characteristic properties of aromatic compounds.—(i) The aromatic substances, as a rule, contain a higher percentage of carbon and a lower percentage of hydrogen than the corresponding aliphatic compounds. They, therefore, burn with a sooty flame like acetylene. Thus benzene, C_6H_6 , contains 92.3% carbon but hexane, C_6H_{14} , only 83.7%. They are, however, remarkably stable and do not behave as unsaturated compounds in many respects.

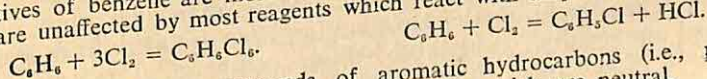
(ii) With conc. H_2SO_4 , aromatic compounds generally form sulphonic acids; this is practically unknown in aliphatic chemistry.



(iii) Conc. HNO_3 usually converts the aromatic hydrocarbons and their derivatives to nitro-derivatives. Direct introduction of a $-NO_2$ group into aliphatic compounds is rather uncommon (but vide p. 173). The aromatic nitro-compounds are reduced to amino-derivatives which form diazo-compounds. Parallel examples in the aliphatic series are rare.



(iv) Chlorine and bromine form addition as well as substitution products with aromatic hydrocarbons, the latter being more common. Monohalogen derivatives of benzene are more stable and so, less reactive, than alkyl halides. They are unaffected by most reagents which react with alkyl halides (pp. 73-75).



(v) The hydroxy compounds of aromatic hydrocarbons (i.e., phenols) are acidic unlike those of paraffins (i.e., alcohols) which are neutral.

The aromatic compounds possess a closed-chain or ring of six carbon atoms, which remains intact in most chemical changes; drastic measures rupture the ring into simpler fragments like CO_2 , oxalic acid, etc. In fact, the fundamental difference between the two groups is the difference in structure, which accounts for the differences in their behaviour.

Conversion of open-chain compounds into closed-chain or aromatic is possible in some cases *e.g.*, acetylene, passed through a red-hot tube, forms benzene (p. 68) and acetone, distilled with conc. H_2SO_4 , yields mesitylene (p. 139). Some aromatic compounds split up into open-chain derivatives, *e.g.*, on careful oxidation, phenol yields meso-tartaric acid and maleic acid is obtained by the catalytic oxidation of benzene (p. 248).

Aromatic compounds are widely distributed in nature. About 75 per cent of known organic compounds are aromatic. Many occur in plants as essential oils, resins, colouring matters, etc., and some in petroleum. Quite a large number are found in, or derived from, coal-tar, a by-product in the manufacture of coal-gas, or coke for metallurgy. A dozen therefrom are the starting materials for hundreds of benzene derivatives. The accidental discovery of the first coal-tar colour, *mauve*, by the eighteen-year-old W. H. Perkin in 1856 while attempting synthesis of quinine, gave the impetus to explore coal-tar products for synthetic dyestuffs; a consequent development of aromatic chemistry rapidly followed. In England coal was first used for lighting in 1787 and the first coal-tar distillery built in 1822.

Destructive distillation of coal.—Bituminous coal (containing about 32-40% volatile matter), heated to $1000-1400^\circ$ out of contact with air in fire-clay or iron retorts, yields

- (i) Coal-gas (about 17% of the weight of coal taken)
- (ii) Ammoniacal liquor (8-10%)
- (iii) Coal-tar (4-5%) and
- (iv) Coke (about 70%).

Hot coal-gas with other volatile products is passed through a series of pipes kept cool by dipping in water, or exposing to the air. The non-volatile residue *viz.*, coke, is mainly used for the extraction of iron from its ores and as fuel. As the gas cools in its passage through upright pipes, much tar and gas-liquor deposit. These are run into large settling tanks where they separate into two layers. The lower, viscous layer (sp. gr. 1.1-1.2) is the coal-tar, the source of many aromatic compounds. The upper ammoniacal liquor is drawn off and worked for making ammonia and ammonium salts. Coal-gas is purified from traces of H_2S , CO_2 , etc. and used as fuel and for illumination.

Coal-tar, once a waste and veritable nuisance, supplies to-day the starting materials for many valuable dyes, drugs, perfumes, explosives, photo-goods, etc. From coke ovens about 10-20 gallons of tar are obtained per ton of coal. More than 300 pure organic compounds, mostly aromatic, have so far been isolated from coal-tar. The coal-tar crudes, containing these compounds, represent only about 0.5% of the coal. About four crores tons of coal are carbonised annually in Great Britain for coke and gas, and the tar produced (18 lacs tons) is largely utilised for the manufacture of various products of every-day-life. More than a lac of people are thus employed. Fairly large quantities of tar are produced in India as well in the gas-works of Bombay and Calcutta or coke-ovens at Jamshedpur and in

other places, but except very recently at Durgapur, few large-scale efforts have been made to recover valuable products therefrom and convert them into dyes, drugs, explosives, plastics, etc.

In Great Britain, about 250 million tons of coal are mined annually, of which 20 and 18 million tons are carbonised for coke and gas respectively. In India, only 45.2 million tons of coal were produced in 1958, of which only a small fraction was coked by the iron industries. More than half of the coal-tar is applied to the roads in Britain; in India, practically all of it is used in road-making. Coke-tar does not materially differ from gas-tar. Since 1940 large-scale underground gasification of coal without shafts (not a single worker is employed underground) has been started in U.S.S.R. With oxygen blast, much cheaper (at $\frac{1}{3}$ the normal cost) gas is produced. 80-90% of the coal (instead of 60% if mined) is thus utilised.

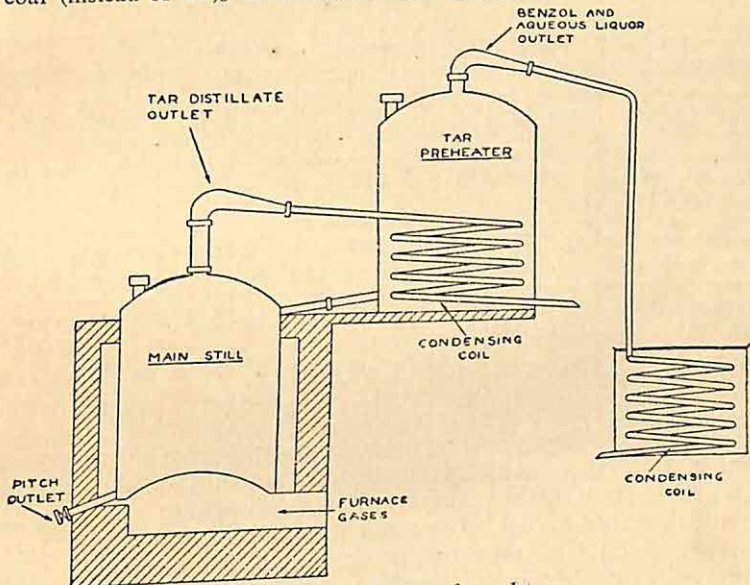


Fig. 48. Distillation of coal-tar.

Distillation of coal-tar.—Besides finely dispersed carbon, to which its black colour is due, coal-tar contains complex substances—acid, neutral and basic—together with varying amounts of water. The in-going charge of tar is dehydrated in a pre-heater by the hot vapour from the distillation itself. First runnings, boiling up to 110° , containing aqueous liquor, benzol, etc., are thus obtained. The tar is transferred to a large, wrought iron still (of 20-30 tons capacity) enclosed in brickwork and heated by direct firing (Fig. 48). The vapours are led through a long iron worm immersed in the tar of the pre-heater. The distillate is condensed and collected in fractions. As distillation proceeds, the temperature gradually rises and the receivers are changed either according to temperature or density of the distillate. A black, somewhat brittle mass called 'pitch' is left in the still. The various fractions collected are shown in p. 318. World production of coal-tar exceeds 10 million tons, about $\frac{2}{3}$ being distilled.

In recent years the industry of low-temperature carbonisation of coal

(between 400-600°) has been developed for obtaining smokeless fuel and oils. About 3 gallons of volatile oil ('crude petrol') are obtained per ton of coal. It is paraffinoid, highly volatile and has good anti-knock properties; the R.A.F. of Britain depended during the last war chiefly on this fuel. Great Britain has no natural petroleum.

The tar (18-20 gallons per ton of coal against 9-10 gallons in high temperature carbonisation) also has a different composition, consisting of about 50% neutral paraffinoid oils, 20% phenolic bodies and 30% resinoids. Benzene, naphthalene, anthracene, etc. occur in minute quantities. These begin to form at about 750° through the pyrogenic decomposition of ethylenes and acetylenes formed at intermediate stages. So, for benzene and other aromatic compounds, low-temperature tar is a poor source.

Fractions of coal-tar distillation

Fraction	Temp. of distillation	Approx. sp. gr.	Approx. yield %	Main constituents
Light oil or crude naphtha	up to 170°	0.92	7-8	Benzene & homologues
Middle oil or carbolic acid	170°-230°	1.01	8-10	Phenol & naphthalene
Heavy oil or creosote oil	230°-270°	1.04	8-10	Cresols
Anthracene oil or green oil	270°-360° or higher	1.10	16-20	Anthracene, carbazole & phenanthrene
Pitch	left in the still	—	50-60	Carbon

Pitch, 92-94% of which is carbon, is run out of the still *before* solidification. It is mainly employed in road-making and as a binder for coal-briquettes, a fuel. Dissolved in naphtha, pitch (together with coumarone resin) is a protective paint. Pitch is also used for roofing. 'Anthracene oil' gives, on cooling, anthracene, $C_{14}H_{10}$, which is separated by vacuum filtration and purified for making dyes. 'Heavy oil' is a preservative for timber, and a fuel for Diesel engines. It contains phenols and cresols to which its protective action is due. 'Middle oil' consists mainly of carbolic acid and naphthalene. On cooling, naphthalene crystals readily separate; these are removed by pressing out the oil, and purified. The oil is worked out for carbolic acid. The disposal of tar is economic if benzene, carbolic acid, cresols, creosote oil, pitch and refined tar have a good market.

Treatment of light oil.—The first distillate, a brownish yellow liquid (sp. gr. 0.92), contains neutral bodies such as benzene, toluene, etc., acid substances like phenol, basic pyridine, aniline, etc., a little water and thiophene, C_4H_4S . The oil is re-distilled, and the distillate below 70° rejected. The rest of the distillate, having about 65% of benzene, is agitated with conc. H_2SO_4 , when aniline, pyridine and most of the thiophene dissolve. The acid layer from the bottom is drawn off, and the oil treated with caustic soda solution (7-10%) which removes carbolic acid and any residual H_2SO_4 . It is washed

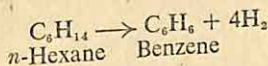
neutral with water, and re-distilled from a steam-heated iron still with a long fractionating column. The distillate is collected in three fractions according to temperature, *viz.*, (i) 90's benzol, (ii) 50's benzol, and (iii) solvent naphtha.

'90's Benzol' means that 100 c.c. of this, if distilled, will yield 90 c.c. distillate below 100°. Actually it contains 84% benzene, 13% toluene and 3% xylenes. Similarly '50's benzol' contains about 46% benzene. These are fractionated to obtain benzene. 'Solvent naphtha' is an industrial solvent for rubber (*e.g.*, in making water-proofs) and also an illuminant. The portion coming at 80°-82° during fractionation of '90's benzol', is moderately pure benzene having a little toluene and thiophene. The distillate is cooled in a freezing mixture, benzene solidifies at 5.4° and is separated from the still-liquid impurities. It is redistilled and obtained practically pure, containing only traces of thiophene, C_4H_4S , (b.p. 84°).

Thiophene resembles benzene so closely that separation is difficult. It may be removed by boiling commercial benzene with mercuric acetate or, by treating alternately with cold and hot conc. H_2SO_4 , followed by distillation. Thiophene is more readily sulphonated than benzene. It is detected by *indophenin reaction*: A crystal of isatin is dissolved in a little cold conc. H_2SO_4 and shaken with a few c.c. of coal-tar benzene. A deep blue colour of indophenin indicates thiophene. Crude benzene may contain up to 0.5% of it.

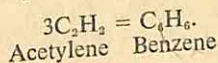
Benzene, C_6H_6 , was discovered by Faraday in 1825 in the illuminating gases made by the destructive distillation of whale oil. In 1834 Mitscherlich, a German chemist, prepared it from benzoic acid (obtained from gum benzoin) whence the name. In 1845 Hofmann isolated it from coal-tar which had already been shown to contain naphthalene in 1819 and anthracene in 1832. 'Benzine' or 'benzoline' is a mixture of low-boiling paraffins from petroleum. Benzene occurs in Californian petroleum.

Benzene is obtained from coal-tar by fractionation as already described; the yield is about 2 gallons per ton of coal distilled. It is also recovered from coke-oven gas either by scrubbing with a heavy tar oil or adsorbing with active charcoal, the dissolved or adsorbed benzene is liberated by steam distillation. Benzene and its homologues are made from straight-run gasoline in U.S.A. The particular fraction is passed through V_2O_5 supported on Al_2O_3 at 500° and 10-20 atmospheres; *n*-hexane gives benzene, *n*-heptane yields toluene and *n*-octane forms xylene and ethylbenzene. The process, called hydroforming (as hydrogen is added to the in-going vapour to keep the catalyst active) involves cyclisation and dehydrogenation:

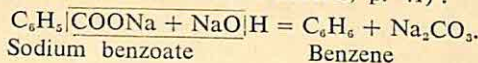


The following methods are of academic interest only.

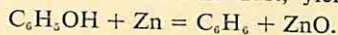
Preparation.—(1) By passing acetylene through a dull-red hot tube, benzene with other aromatic hydrocarbons may be synthesised (p. 68):



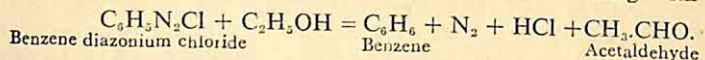
(2) By distilling sodium benzoate with soda-lime, benzene is obtained (cf., preparation of methane from sodium acetate, p. 41):



(3) Phenol, $\text{C}_6\text{H}_5\text{OH}$, distilled with zinc dust, yields benzene:

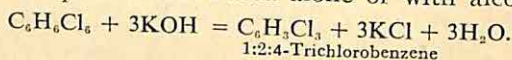


(4) Benzene diazonium chloride forms benzene on boiling with alcohol:



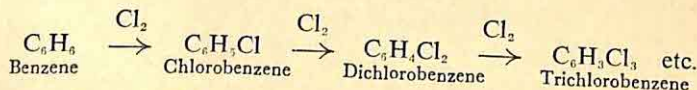
Properties.—Benzene is a colourless, mobile and highly refractive liquid (b.p. 80.4°) with a sharp smell. It has a sp. gr. 0.87 (at 20°). Solidified benzene melts at 5.4° . It is highly inflammable and burns with a smoky luminous flame. Benzene is practically immiscible with water but miscible with many organic liquids such as ether, alcohol, etc. It is a good solvent for fats, resins, gums, rubber, etc., as also for iodine, phosphorus, sulphur, etc. Toluene which is less toxic, is preferred to benzene as a solvent. Two parts of benzene vapour in about 100 parts of air may prove fatal if inhaled; absorption of benzene, liquid or vapour, through the skin has toxic effects. Though unsaturated, it is remarkably stable. It does not decolorise bromine-water or potassium permanganate solution. Nickel cyanide-ammonia complex quantitatively absorbs benzene and is employed for estimating benzene in a gas mixture.

Reactions.—(1) In ultra-violet light or direct sunlight, benzene forms additive products with chlorine and bromine; benzene hexachloride, $\text{C}_6\text{H}_6\text{Cl}_6$, and hexabromide, $\text{C}_6\text{H}_6\text{Br}_6$, are finally formed at 50 – 60° . These decompose when heated alone or with alcoholic potash:



Eight benzene hexachlorides are theoretically possible (cf. inositol, p. 314) depending upon the position of the H and Cl atoms on either side of the plane of the benzene ring. Of the seven known isomers, the gamma (gammexane, BHC or 666, m.p. 111°) is the most powerful insecticide. Faraday first prepared benzene hexachloride in 1825 but the insecticidal property was discovered in around 1942. In 1955, U.S.A. made 49 million lb. of gammexane. The γ -isomer, representing about 15% of the mixture of hexachlorides, is more soluble in benzene than others, and reported to be odourless. It acts more quickly than D.D.T.

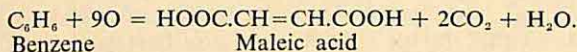
(2) In presence of a 'halogen-carrier' such as iron, AlCl_3 , or iodine, benzene forms substitution products with chlorine and bromine at ordinary temperature. Gradually, all the hydrogen atoms can thus be replaced; the process can be controlled (cf. chlorination of methane, p. 43).



Iodine gives iodobenzene at high temperature and in presence of oxidising agents, e.g., HIO_3 , HNO_3 , FeCl_3 or HgO which decompose the HI as soon as formed (cf., methyl iodide, p. 71).

(3) On passing benzene vapour and hydrogen over finely-divided nickel at about 200°, cyclohexane, C_6H_{12} , (p. 313) is obtained (*cf.* formation of ethane from ethylene, p. 58). The double bonds are reduced one by one, the first being more difficult to reduce than the other two. Cyclohexane and methylcyclopentane result on heating benzene with hydriodic acid at 250°.

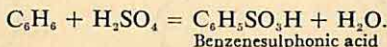
(4) Air in presence of vanadium pentoxide oxidises benzene to maleic acid (p. 248). Chromic acid or acid pot. permanganate very slowly decomposes it to carbon dioxide and water.



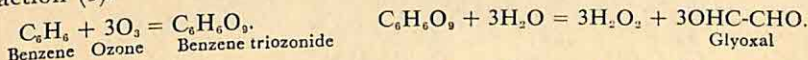
(5) Conc. HNO_3 below 70° nitrates benzene, more readily in presence of conc. H_2SO_4 (which apparently takes away the water formed), to nitro-benzene, replacing a H atom by a $-NO_2$ group. At higher temperature and with excess of HNO_3 , dinitrobenzene, $C_6H_4(NO_2)_2$, results.



(6) Unlike paraffins, benzene yields benzenesulphonic acid when heated with conc. H_2SO_4 . With fuming H_2SO_4 , benzenedisulphonic acid, $C_6H_4(SO_3H)_2$, is formed:



(7) With ozone, benzene *slowly* forms benzene triozonide (*cf.* ethylene ozonide, p. 59) which, on hydrolysis, gives three molecules of glyoxal. This indicates the unsaturated nature of benzene, as does reaction (3).



(8) On passing benzene vapour through a tube at 700°-800° or through molten lead, diphenyl is formed.



The monovalent radical $C_6H_5\cdot$ is called 'phenyl' from 'phene' (to shine), an obsolete name for benzene. It corresponds to alkyl radicals like $CH_3\cdot$ or $C_2H_5\cdot$; aromatic hydrocarbon radicals are commonly known as aryl radicals.

Uses.—Benzene is an excellent solvent for rubber, resins, fats, oils and grease. It is used in dry-washing. Nitrobenzene, phenol, styrene and cyclohexane are made from benzene. Mixed with petrol, benzene (it has a high anti-knock value) is a motor fuel. It is a laboratory reagent, *e.g.*, in cryoscopic determination of mol. wts., in the extraction of organic compounds, etc. Benzene kills fleas, lice, etc.

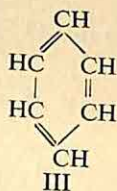
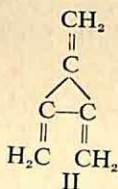
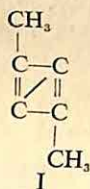
In 1955 U.S.A. produced 410 million gallons of benzol, but India's annual output is only 2,417,000 gallons of 90's benzol. In U.S.A. about 35% of the benzene produced is used for making styrene, 20% for phenol, 5% for aniline and the rest for Nylon, maleic acid, insecticide, etc.

Constitution of benzene.—(i) From analysis and mol. wt. determination, benzene is C_6H_6 .

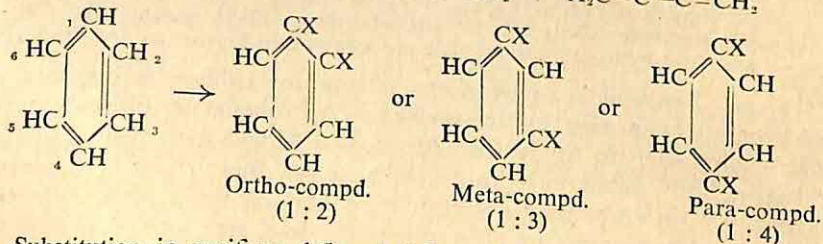
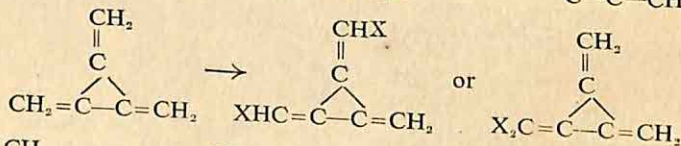
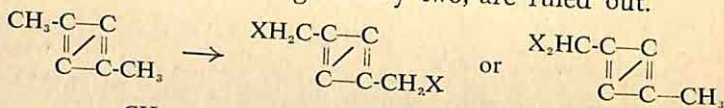
(ii) Compared with hexane, C_6H_{14} , it is highly unsaturated. Benzene, however, exhibits only some of the characteristics of unsaturated compounds, *viz.*, it adds on chlorine giving finally benzene hexachloride, $C_6H_6Cl_6$; gives cyclohexane, C_6H_{12} , on catalytic hydrogenation and forms a triozonide, $C_6H_6O_9$, (p. 321). These indicate three double bonds in the molecule.

(iii) Benzene is quite stable and behaves like saturated compounds *e.g.*, it does not decolorise bromine-water or react with alkaline $KMnO_4$ in the cold; forms substitution products such as $C_6H_5Cl_3$ with chlorine under suitable conditions and does not add on hypochlorous acid or halogen hydrides. The double bonds in benzene are not, therefore, of the ethylenic type.

(iv) Benzene forms only *one* monosubstituted product such as chlorobenzene, C_6H_5Cl , or nitrobenzene, $C_6H_5NO_2$. This means that the hydrogen atoms of benzene are symmetrically situated *i.e.*, equivalent to one another. Benzene should, therefore, have a ring structure such as



(v) But since benzene forms *three* disubstituted derivatives, $C_6H_4X_2$, I and II which can give only two, are ruled out.



Substitution in positions 1:5 and 1:6 would be the same as 1:3 and 1:2 respectively (Greek *ortho* adjacent, *meta* the next position beyond, *para* across).

Benzene, therefore, has structure III suggested by August Kekulé (1829-1896), a German chemist, in 1865 in his celebrated 'Benzene

Theory' which has, it may be truly said, 'revolutionised' organic chemistry. The number of known organic compounds was about 3,000 in 1865, by 1910 it became about 2 lacs. There are two objections against the Kekulé formula *viz.*, benzene is remarkably stable though it has three double bonds, and it gives only *one* ortho-derivative though positions 1:2 and 1:6 are not identical (one having a single and the other a double bond between the carbon atoms). Alternate structures have been suggested from time to time. The difficulty about the Kekulé formula is the disposal of the fourth valency of carbon. This has been done in various ways. Claus in 1867 put forth his diagonal formula in which the carbon atoms within the ring are diagonally linked; two years later Ladenburg, working in Kekulé's laboratory, proposed the prism formula:



Fig. 49.
Claus's diagonal formula.

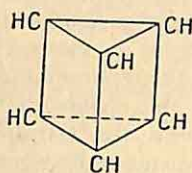


Fig. 50.
Ladenburg's prism model.

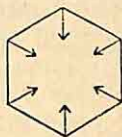
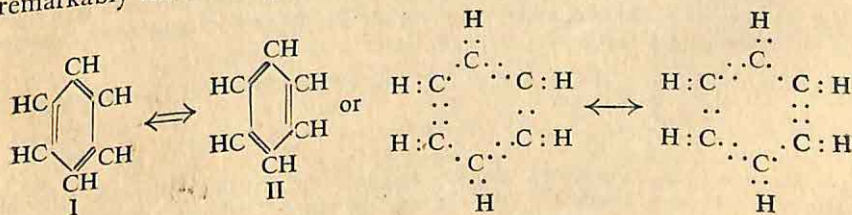


Fig. 51
Centric formula of
Armstrong and Baeyer.

As neither has a double bond, formation of triozone cannot be explained. The single linkages do not easily fit in the tetrahedral carbon atom, the angle between valences being $109^{\circ}28'$. Ladenburg's formula which is three-dimensional, fails to explain the formation of cyclohexane from benzene by reduction; it also would make some trisubstituted derivatives asymmetric *i.e.*, optically active, which is not a fact.

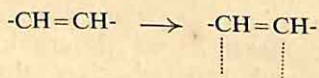
A centric formula came from Armstrong (1887) and Baeyer (1888) almost simultaneously. Here the valencies are directed towards the centre of the ring, balancing one another. The idea is to account for the stability of benzene, and also why partly reduced benzene (*e.g.*, dihydrobenzene) behaves more or less as an olefine. Kekulé modified his views in 1872 suggesting that the double bonds were *continuously* changing positions, *i.e.*, they were dynamic rather than static. The tautomeric forms I and II are in equilibrium. The difference between 1:2- and 1:6-derivatives thus disappears. This remarkably fits in the present concept of resonance.



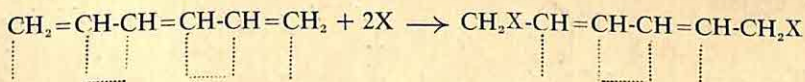
It is now believed that neither I nor II but an intermediate state—a hybrid structure—called *resonance structure* (which cannot, however, be depicted on the paper) represents the normal state of the molecule. A crude analogue is a mule—a hybrid between a horse and a donkey—which is neither a horse nor a donkey but something intermediate between the two, possessing some characters of each. A hybrid may also be compared with a green impression formed by printing a blue pattern on an identical yellow one; the single green hybrid results from the merged yellow and blue patterns. Resonance between two (or more, as in the case of naphthalene or anthracene) structures corresponding to the same atomic arrangement but to different electronic distribution, largely stabilises the molecule. The greater strength of the linkages, due to resonance (or *mesomerism*), is accompanied by a shortening of the bond distance. Each carbon-carbon linkage assumes the characteristics similar to those of a double bond, each bond between two C-atoms is intermediate in character between a single bond and a double bond; resonance energy (about 38 k. cal.) makes it more stable. All the atoms in the molecule are coplanar, and the bond angles approach the tetrahedron angles. This agrees with the fact that the bond distance between any two adjacent C-atoms in benzene (this can be accurately measured) is the same (viz. 1.39 Å) and is intermediate between the values for a single (1.54 Å) and a double bond (1.34 Å). (Angstrom unit, Å, = 10^{-8} cm.). The stability of the aromatic nucleus and the absence of ethylene reactivity are thus explained.

Tetra- and di-hydrobenzene, on hydrogenation, yield cyclohexane, evolving 28.6 and 55.4 k.cal. of heat respectively. Benzene forms cyclohexane liberating only 49.8 k.cal. and not 85.8 as expected from a simple triene. The difference (36 k.cal.) represents the resonance energy that stabilises benzene.

Thiele (1865-1918), to explain the characteristics of compounds with alternate single and double bonds (which he named 'conjugated double bonds' such as $-\text{CH}=\text{CH}-\text{CH}=\text{CH}-$), advanced his *theory of partial valency* in 1899. He assumed that in ethylene linkages of such compounds, the full valency forces were not utilised but a portion remain free, which he graphically indicated by dotted lines:



According to him, in a conjugated system, these partial valencies neutralise one another and addition takes place mainly at the end carbon atoms, which is an experimental fact.



Benzene has conjugated double bonds; the partial valencies are all neutralised by one another. There is no free partial valency and so benzene behaves as a stable compound, notwithstanding the unsaturation.

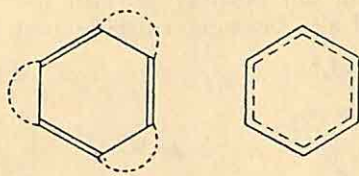
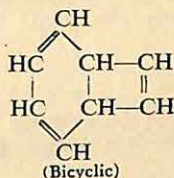
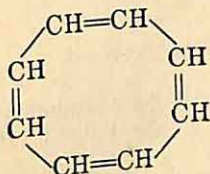
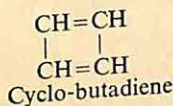


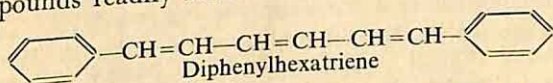
Fig. 52.—Benzene with partial valencies neutralised.

But conjugated double bonds alone do not possibly make benzene so stable as cyclo-octatetraene (a yellow compound prepared by Willstätter), having a similar structure, behaves as a typical unsaturated compound (combines with HBr, for example, and is readily decomposed or oxidised). Cyclobutadiene, with a similar structure, is too unstable to be isolated. Doubts were expressed if the compound obtained by Willstätter was really cyclo-octatetraene. During the last war cyclo-octatetraene was manufactured in Germany by polymerising acetylene in tetrahydrofuran in presence of ethylene oxide at 80° and 20 atmospheres pressure. Nickel cyanide was the catalyst. It is a gold-yellow liquid, boiling at 142-43° at atmospheric pressure and is quite stable. It is now believed to have a bicyclic structure. The bond lengths in the molecule are 1.34 Å for double bond and 1.54 Å for single bond; the molecule is not, therefore, stabilised by resonance. It does not possess aromatic properties.



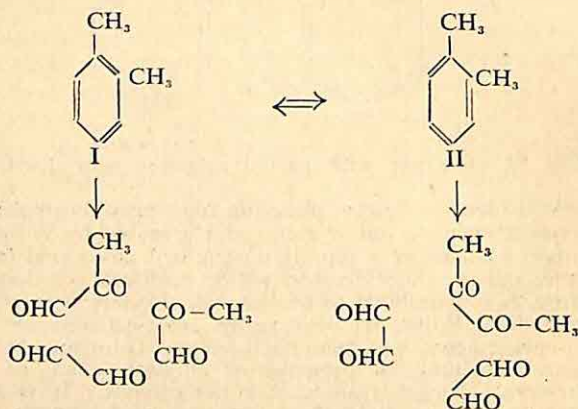
Cyclo-octatetraene

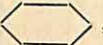
A strong evidence in favour of Thiele's theory is, however, the inertness of diphenylhexatriene to reagents with which ordinary ethylenic compounds readily react.



The two-dimensional hexagonal formula of Kekulé has, therefore, been retained as the best. Some interesting physical studies support the same. The X-ray crystal analysis of benzene derivatives reveals that the carbon atoms of benzene lie in one plane, while Raman spectra indicate the symmetry of the benzene molecule and suggest that the ring is planar and has double bonds. Parachor values of benzene and its derivatives point to the existence of three double bonds and a six-membered ring. Kekulé's idea that the double bonds in benzene are constantly oscillating between the structures I and II (p. 323) has been supported by experimental facts after 60 years. Ortho-xylene, a resonance hybrid like benzene, gives on ozonisation and hydrolysis (i) glyoxal, $\text{OHC} \cdot \text{CHO}$, (ii) methylglyoxal, $\text{CH}_3 \cdot \text{CO} \cdot \text{CHO}$, and (iii) dimethylglyoxal or diacetyl, $\text{CH}_3 \cdot \text{CO} \cdot \text{CO} \cdot \text{CH}_3$. Of these, (i) and (ii) can result from Kekulé structure I and (i) and (iii) from the other structure

II but neither alone can possibly furnish all the three fragments. Hence *o*-xylene (and also benzene) exists in both the forms.



Generally, a plane hexagon, , is used to represent benzene. For the facility of remembering the positions in the ring, the hexagon is sometimes slightly elongated.

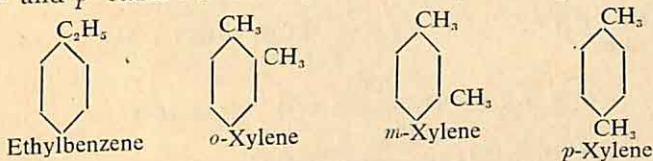
QUESTIONS

1. State the evidence on which the constitution of benzene is based. What are the modern views about its constitution? (B.A. Degree Exam., 1942, Madras Uni.).
2. In what way is the strength of the valency bond between two atoms affected by the form of the molecule? Illustrate your answer by examples from organic chemistry. (Inst. of Patent).
3. Compare the properties of benzene with those of hexane and cyclohexane.
4. How can pure benzene be obtained synthetically? What are its typical reactions which distinguish it from aliphatic compounds?
5. What are the products of distillation of coal-tar? How is commercial benzene prepared from it? Explain the terms 'benzol' and 'benzine'.
6. What is Thiele's theory of partial valency? Why should the theory be not accepted to explain the constitution of benzene?
7. By what general properties are aromatic compounds distinguished from aliphatic compounds? Discuss the merits and demerits of Kekulé's formula for benzene. (B.Sc. Pass, 1934, Allahabad Uni.).
8. Write what you know about the method of coal-tar distillation and the different fractions obtained. (B.Sc. Pass, 1938, Calcutta Uni.).
9. Discuss the constitution of benzene. (B.Sc. Subsidiary, 1938, Bombay Uni.; B.Sc. 1943, Benares Hindu Uni.; B.Sc. 1947, Nagpur Uni.; B.Sc. 1952, Gauhati Uni.; B.Sc. Pass, 1953, Lucknow Uni.).

CHAPTER XXXII

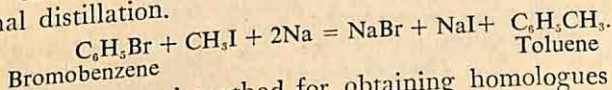
THE HOMOLOGUES OF BENZENE

Benzene and its homologues, the simplest of aromatic hydrocarbons, are represented by the general formula, C_nH_{2n-6} . The homologues are alkylbenzenes; e.g., toluene is methylbenzene, $C_6H_5.CH_3$. It has no isomer; but ethylbenzene, C_8H_{10} , has three (*o*-, *m*- and *p*- stand for ortho-, meta- and para- respectively):

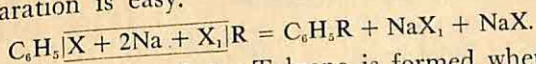


Toluene, toluol, methylbenzene or phenylmethane, $C_6H_5CH_3$, was obtained by the dry distillation of *Tolu balsam*, whence the name. The chief source is, however, the coal-tar distillate (light oil) wherefrom it is isolated by fractional distillation. About 0.4 gallon of toluene is obtained per ton of coal distilled. It also occurs in some petroleum (e.g. in Assam or Borneo oil). Crude petroleum seldom contains more than 1% of toluene by volume. *n*-Heptane (from petroleum) passed over chromic oxide at 500° , gives toluene. U.S.A. makes toluene also by passing methylcyclohexane (from petroleum) under pressure over molybdena-alumina at 560° to meet the extra demand. In 1955 she made 334 million gallons of toluene, 45% being from petroleum. Aromatic hydrocarbons, unlike the aliphatic, dissolve in liquid sulphur dioxide or dimethyl sulphate; this is utilised in petroleum refining. Toluene may be obtained by synthetic methods:

(1) **Fittig's method.**—When a dry ethereal solution of bromo- or iodobenzene and methyl iodide is treated with metallic sodium, toluene is formed. Sodium in thin slices is added to the ethereal solution, with cooling if necessary. The liquid is filtered from the insoluble sodium salts, ether evaporated off, and pure toluene obtained by fractional distillation.

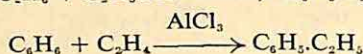
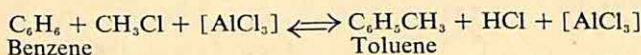


This is a general method for obtaining homologues of benzene; any alkyl group can thus be introduced. Iodo- and bromo-derivatives are more reactive than chloro-. It is an extension of Wurtz synthesis of paraffins (p. 74) and sometimes called *Wurtz-Fittig reaction*. Here sodium removes the halogen simultaneously from an alkyl and an aryl halide. $R-R$ and $C_6H_5-C_6H_5$ also result. Their b.p. being widely different, separation is easy.

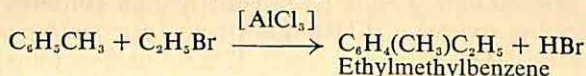


(2) **Friedel-Crafts reaction.**—Toluene is formed when an excess of benzene is treated at ordinary temperature with a methyl halide in presence of *anhydrous*, finely powdered $AlCl_3$. Halogen hydracid is

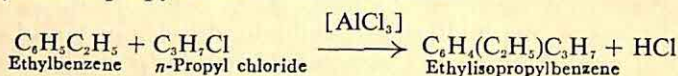
liberated during the reaction. All reagents must be dry. Methane and chlorobenzene, C_6H_5Cl , do not, however, yield toluene. The reaction is reversible; the alkyl group may get detached at high temperature. It is not always possible to arrest the reaction at a desired stage. Aliphatic alcohols and olefines may also serve as alkylating agents. C. Friedel and J. M. Crafts, working under Wurtz in Paris, discovered the reaction in 1877. Recently, benzene has been made to react with an alkyl halide under pressure without a catalyst, and some aliphatic and alicyclic compounds have been subjected to Friedel-Crafts reaction.



The product is treated with water and the lighter hydrocarbon layer is fractionally distilled to obtain toluene. The method is important and generally employed for the synthesis of other homologues of the series. The methyl group may migrate; thus toluene and $AlCl_3$ give benzene and xylene, $C_6H_4(CH_3)_2$.

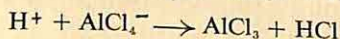
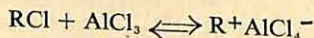


Alkyl halides generally isomerise during the condensation; *n*-propyl halides yield isopropylbenzene with benzene.

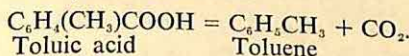


Anhydrous $AlCl_3$ may be replaced by $FeCl_3$, BF_3 or $ZnCl_2$, but they are less efficient. With large excess of alkyl halide and by prolonging the reaction, di-, tri-, etc. alkyl derivatives are formed. Aromatic hydrocarbons react also with acid chlorides in presence of $AlCl_3$ to form ketones (q.v.).

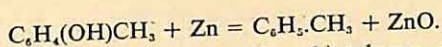
The mechanism of Friedel-Crafts reaction is not yet well established. According to a widely accepted view, $AlCl_3$ in the first step forms with the alkyl (or acyl) halide a strongly polar complex, $R^+AlCl_4^-$, as an intermediate product. Such addition compounds have actually been isolated in several cases; all the four Cl-atoms in the $AlCl_4^-$ ion have also been shown to be equivalent. Electrophilic carbonium ion, R^+ , now attacks the benzene nucleus with the liberation of H^+ . The latter and $AlCl_4^-$ combine to yield $AlCl_3$ and HCl .



(3) Toluic acid (*o*-, *m*- or *p*-), on distillation with soda-lime, gives toluene as benzoic acid yields benzene.

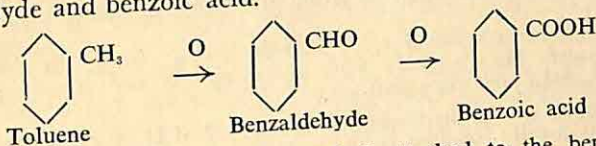


(4) Hydroxytoluenes (*o*-, *m*- or *p*-cresol), reduced with zinc dust, form toluene (cf., phenol giving benzene, p. 320). The yield is poor.



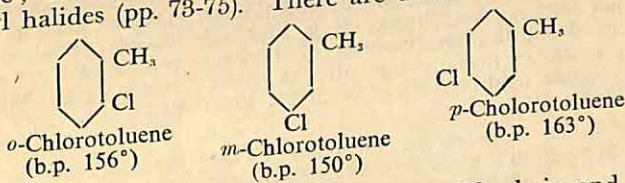
Like benzene, coal-tar toluene contains thiotoluene or methylthiophene, $\text{C}_6\text{H}_4\text{S}$, which also gives indophenin reaction, and is difficult to remove.

Properties.—Toluene is a colourless liquid (b.p. 110° , sp. gr. 0.869 at 20°) which solidifies at -98° . It is immiscible with water, and closely resembles benzene in its behaviour. On catalytic hydrogenation, toluene gives hexahydrotoluene, $\text{C}_6\text{H}_{11}\text{CH}_3$. Unlike benzene, its homologues are susceptible to oxidation. Chromic acid or pot. permanganate oxidises toluene directly to benzoic acid; mild oxidising agents (e.g., chromyl chloride) under suitable conditions, produce benzaldehyde. Selenium dioxide at 250° – 340° converts toluene to benzaldehyde and benzoic acid.



The alkyl group or any carbon radical attached to the benzene ring, is known as 'side-chain.' Groups such as $-\text{OH}$, $-\text{NH}_2$, etc. are not regarded as side-chains; thus phenol, $\text{C}_6\text{H}_5\text{OH}$, or nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$, has no side-chain. A side-chain, however long, on oxidation finally becomes a carboxyl group. Thus, ethyl-, butyl- or any alkylbenzene, when oxidised, yields benzoic acid. The longer the side-chain, the easier to oxidise.

Passed into toluene *in the cold* in presence of halogen-carriers like I_2 , P , Fe , chlorine goes to the benzene nucleus and chlorotoluenes (*o*- and *p*-) are formed. By prolonging the passage of chlorine, di-, tri-, etc. chlorotoluenes are obtained. Chlorotoluenes behave like chlorobenzene; the chlorine atom cannot be replaced by $-\text{OH}$, $-\text{CN}$, etc., as in alkyl halides (pp. 73-75). There are three monochlorotoluenes:



Led into *boiling* toluene, it enters the side-chain and replaces the hydrogen of $-\text{CH}_3$ one by one. We thus get (i) benzyl chloride, $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ (isomeric with chlorotoluenes), (ii) benzal (or benzylidene) chloride, $\text{C}_6\text{H}_5\text{CHCl}_2$, and (iii) benzenyl chloride or benzotrichloride, $\text{C}_6\text{H}_5\text{CCl}_3$. ($\text{C}_6\text{H}_5\text{CH}_2\cdot$ is benzyl radical, $\text{C}_6\text{H}_5\text{CH}=\text{benzal}$ or benzylidene and $\text{C}_6\text{H}_5\text{C}\equiv\text{benzenyl}$). These behave like alkyl halides, the halogen being replaceable by different atoms or groups such as $-\text{OH}$, $-\text{NH}_2$, $-\text{CN}$, etc. (pp. 73-75). Toluene is nitrated more easily than benzene by conc. HNO_3 and *o*- and *p*-nitrotoluenes are mainly formed; the final product of direct nitration is trinitrotoluene (T.N.T.). Similarly, conc. H_2SO_4 gives ortho- and para-toluenesulphonic acids. Toluene forms no addition compound with chlorine.

Constitution of toluene follows from its preparation from benzene or bromobenzene—it is methylbenzene. Oxidation of toluene to benzoic acid confirms this structure.

Uses.—The high explosive, T.N.T. is made from toluene; other nitrotoluenes are used for making some drugs (e.g., novocaine) and dyestuffs. Toluene is a good anti-freeze (it freezes at -98°) for petrol and benzene. It is the starting material for saccharin, and also used in printing inks. It is a commercial solvent, specially for protective coating resins, and also a motor fuel for its high anti-knock property (its octane number is more than 100).

Crum-Brown and Gibson rule.—When toluene is chlorinated in the cold, three different chlorotoluenes ought to result but actually we get ortho- and para-derivatives but no meta-. If, however, mononitrobenzene is further nitrated, *m*-dinitrobenzene is chiefly obtained and very little of the ortho- or para-compound. Crum-Brown and Gibson (1892) suggested an empirical rule for the entrance of a new atom or group into benzene having a substituent X, viz.,

If the hydrogen compound of X is readily and directly oxidisable to the hydroxy-compound, the entering group takes up the meta-position; otherwise it goes to the ortho- and para-positions.

For example, as the hydrogen compound of $-\text{CH}_3$ (i.e., methane) cannot be readily and directly oxidised to the hydroxy-compound (i.e., methyl alcohol), on nitration, the $-\text{NO}_2$ group enters the ortho- and para-positions in toluene. Similarly, mono-substituted benzenes having Cl, Br, I, $-\text{NH}_2$, $-\text{OH}$ or any alkyl group, give *o*- and *p*-isomers mainly. On the other hand, nitrobenzene, on chlorination, forms *m*-nitrochlorobenzene inasmuch as the hydrogen compound of $-\text{NO}_2$ can directly be oxidised to the hydroxy-compound, viz., nitric acid, HONO_2 . If any of $-\text{NO}_2$, $-\text{CHO}$, $-\text{COOH}$, $-\text{HSO}_3$, $-\text{CN}$, etc., be already present in the benzene ring, chiefly *m*-isomers result. It may be noted that the latter radicals, unlike the former, contain a double or a triple bond. *o*- and *p*-substitutions, as a rule, proceed more easily than *m*-substitutions. This is not explained by the rule.

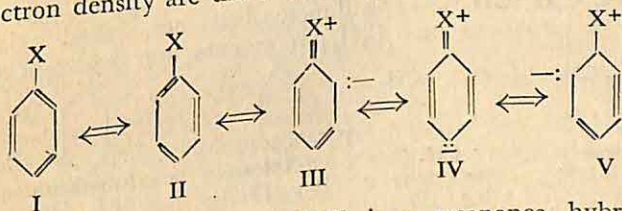
It predicts the formation of *m*-nitrochlorobenzene by chlorinating nitrobenzene but not by nitrating chlorobenzene; *o*- and *p*-nitrochlorobenzene are obtained in the latter case. Crum-Brown and Gibson rule has been a valuable guide, but is not without exceptions. It is silent about the formation of tri-derivatives from di-substitution products of benzene containing two different groups. Then again, in many cases, all the three di-derivatives have been isolated, e.g., benzoic acid, on nitration at 0° , gives 80.2% *m*-, 18.5% *o*- and 1.3% *p*-nitrobenzoic acid.

Furthermore, the relative proportions of the di-substituted isomerides formed have been found to depend not only upon the substituent already present but also, to a certain extent, on the entering group or element as well as the experimental conditions. Thus, fluorobenzene, on nitration at 0° yields 12.4% *o*- and 87.6% *p*-compounds; but chlorobenzene under the same condition, gives 30% *o*- and 70% *p*-isomers. Here the existing group influences the yield. Phenol, $\text{C}_6\text{H}_5\text{OH}$, on chlorination, gives almost equal amounts of *o*- and *p*-isomers; but on bromination, gives about 90% *p*- and 10% *o*-compounds. Here the entrants largely determine the yield. Lastly, toluene, on sulphonation, at 0° and 100° produces 53.5% and 72.5% para-derivatives respectively. The *m*- and *o*-products also vary in amount under these conditions. Aniline, $\text{C}_6\text{H}_5\text{NH}_2$, on nitration in presence of a large excess of conc. H_2SO_4 , yields mainly the meta-compound—which is against Crum-Brown Gibson rule. It is difficult to decide what is really meant by 'the hydrogen compound of the existing group being directly oxidisable to its hydroxy-compound.' For example, the hydrogen compound of $-\text{CH}_3$, viz., methane, CH_4 , (in fact, of most other groups) can be directly oxidised to the hydroxy-compound, viz. methyl alcohol, CH_3OH , under suitable conditions (p. 44). But Crum-Brown Gibson rule is based on its not being directly oxidisable.

Hammick and Illingworth's rule (1930), also empirical, states: If in the mono-substituted benzene, $\text{C}_6\text{H}_5\text{-XY}$ (XY representing a radical of two ele-

ments, X being directly linked to the benzene ring), Y be in a higher group in the periodic table than X, or if Y has a lower at. wt. than X (in case they belong to the same group), a meta-derivative is obtained when an element or radical enters the ring. In other cases, including that in which a single atom is present in place of XY, *o*- and *p*-isomers are formed. Thus, nitrobenzene is present in place of XY, *o*- and *p*-isomers are formed. Thus, nitrobenzene (N in group V, and O in group VI), on further nitration, gives meta-dinitrobenzene; cyanobenzene, C_6H_5-CN , for the same reason gives, on chlorination, *m*-chlorocyanobenzene. Toluene, on the other hand, yields *o*- and *p*-nitrotoluene. According to Vorländer, if X of C_6H_5X is electro-positive, it is meta-directing while negative groups are *o*- and *p*-directing.

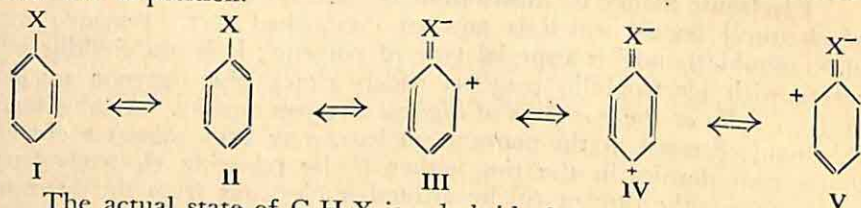
Electronic theory of substitution is based on the electrical character of chemical bonds, which is now an established fact. Benzene with 'three double bonds' is a special type of polyene; it is nucleophilic and reacts with electrophilic reagents which attack the benzene nucleus preferentially at the positions of highest electron density. A substituent X, already present in the benzene nucleus, may bring about a change in electron density in the ring either (i) by releasing electrons from itself towards the ring or (ii) by attracting electrons from the benzene ring towards itself. In case (i), the electron density in the benzene nucleus as a whole is greater than normal, and consequently, C_6H_5X becomes more reactive than benzene, facilitating further substitution. For instance, nitration of toluene, $C_6H_5CH_3$, proceeds nearly 14 times faster than that of benzene. Due to the unsaturated nature of the benzene nucleus and polarisation of the double bonds, the points of high electron density are the *o*- and *p*-positions as indicated below:



The actual structure of C_6H_5X is a resonance hybrid of the resonating structures I-V. C_6H_5X has a small negative charge at both the *o*-positions, and also at the *p*-position. In addition to the resonance effect, electron density at any of these three positions may also increase at the demand of the attacking electrophilic reagent. As a result, substitution occurs at these positions. The common *o*- and *p*-directing groups and atoms are $-OH$, $-CH_3$, $-NH_2$, halogens, $-OR$, $-NHR$, $-CH_2Cl$, $-NR_2$, $-OCOR$, etc. These are saturated or only weakly unsaturated and except the methyl group, in all cases the atom directly linked with the carbon of the benzene ring, has at least one lone pair of electrons. This forms a double bond between X and carbon in the ring and makes an unshared electron pair available at the *o*- and *p*-positions. The $-CH_3$ group, being electropositive, pushes electrons into the ring by inductive mechanism; these pile up at the *o*- and *p*-positions more than at the *m*-. The halogens, having unshared electrons, selectively supply the electrons to the *o*- and *p*-positions by electromeric mechanism when the attacking electrophilic reagent demands. They being strongly electronegative, attract electrons towards them from all positions in the ring by inductive mechanism—this results

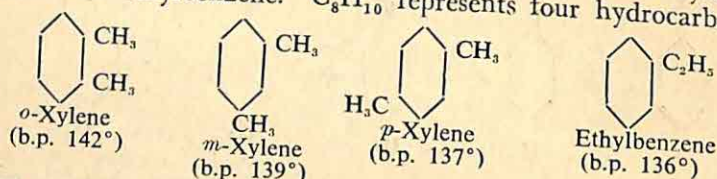
in the deactivation of the benzene nucleus. Further substitution is consequently much more difficult than in the case of benzene.

In case (ii), the substituent X pulls electrons, like halogens, from all positions in the ring. Consequently, the benzene nucleus is deactivated, making further substitution more difficult. The electrons are, however, withdrawn selectively from *o*- and *p*-positions as shown below, leaving the *m*-position practically unaffected, which thus becomes a position of relatively high electron density. Electrophilic reagents, therefore, enter the *m*-position.



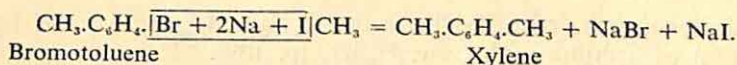
The actual state of C_6H_5X is a hybrid of the resonating structures I-V, the *o*- and *p*-positions have small positive charges and the *m*-position has a relatively high electron density. The common meta-directing groups are $-CHO$, $-NO_2$, $-CN$, $-SO_3H$, $-COOH$, $-CONH_2$, $-COOR$, $-NH_3^+$, $-NR_3^+$, $-COR$, etc. all of which are electron-attracting. Most of them are strongly unsaturated or contain a positively charged atom linked to a carbon in the benzene ring.

Xylenes, $C_6H_4(CH_3)_2$.—The dimethylbenzenes, called xylenes, are isomeric with ethylbenzene. C_8H_{10} represents four hydrocarbons:

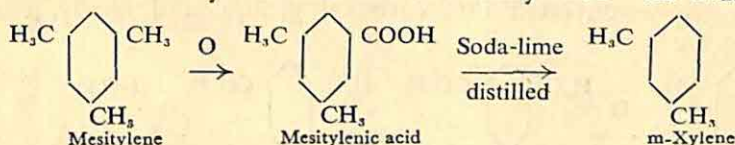


The xylenes occur together, along with benzene and toluene, in the light oil fraction of coal-tar distillation and are obtained therefrom by fractional distillation. A ton of coal yields about 0.2 gallon of xylenes. Their boiling points being very close, they are separated by chemical methods. With conc. H_2SO_4 in the cold, *o*- and *m*-xylenes form sulphonic acids but *p*-xylene remains practically unchanged and is easily removed. The xylenesulphonic acids are then separated by fractional crystallisation of their sodium salts, the *o*-compound crystallising first. The sodium salts are acidified and hydrolysed under pressure separately; *o*- and *m*-xylenes are thus recovered. Hot, dilute HNO_3 oxidises *o*- and *p*-xylene to toluic acids much more readily than the meta. Separation of *m*-xylene is thus possible. Commercial coal-tar xylene contains all the three, the *m*-compound predominating (about 70%). Petroleum xylene is also richest in the *m*-isomer. Pure xylenes are better obtained by synthetic methods:

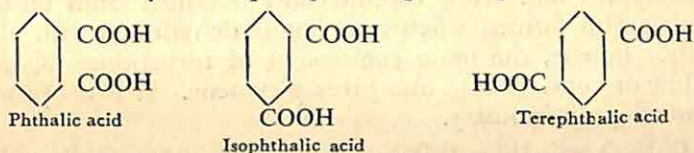
(1) *o*-, *m*- and *p*-xylenes may be prepared by Fittig's method from *o*-, *m*- and *p*-bromotoluenes respectively with methyl iodide and sodium, in the same way as toluene is obtained from bromobenzene (p. 327).



(2) Meta-xylene is conveniently prepared from mesitylene (p. 139) by oxidation to mesitylenic acid and decarboxylation with soda-lime.



Properties.—Xylenes are colourless, inflammable liquids, closely resembling toluene. They are immiscible with water, and volatile in steam. Halogens react with them in the same way as with toluene. Conc. HNO_3 nitrates, and conc. H_2SO_4 sulphonates them. Xylenes differ in their behaviour towards strong H_2SO_4 (mentioned above) and oxidising agents. Hot and dilute HNO_3 oxidises xylenes to monocarboxylic acids—the toluic acids—one of the methyl groups becoming a $-\text{COOH}$ group; *m*-xylene is less readily attacked than the other two. On further oxidation, say, with pot. permanganate phthalic acids result.



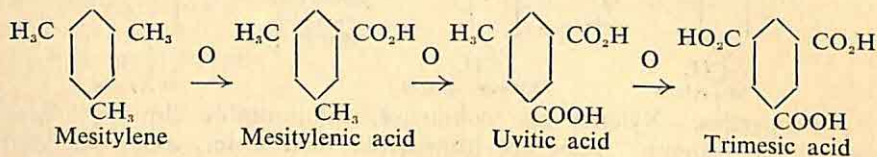
Chromic acid, however, oxidises *p*- and *m*-xylene directly to phthalic acids, and the *o*-compound to carbon dioxide and water. The methyl groups in the *o*-position are difficult to oxidise. Two $-\text{COOH}$ groups in the final oxidation product indicate *two* side-chains in the xylenes. Ethylbenzene gives benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$, on oxidation. For technical purposes, the mixture of xylenes is usually employed in the preparation of lacquer, as solvent for rubber, and motor fuel. Dyes are made from their amino-derivatives.

Identification.—*o*-Xylene gives, on oxidation, phthalic acid which readily forms the anhydride; iso- and terephthalic acids do not form anhydrides. *o*-Xylene can thus be identified. *m*-Xylene alone is obtained from symmetrical mesitylene. So it is known from synthesis. *p*-Xylene is identified by the elimination of *o*- and *m*-isomers. The xylenes can also be identified by their formation from *o*-, *m*- and *p*-bromotoluenes or by Körner's method (p. 334).

Ethylbenzene, $\text{C}_6\text{H}_5\text{C}_2\text{H}_5$, a colourless liquid (b.p. 136°), also occurs in coal-tar, but only to a small extent. It may be prepared either by Fittig's method from bromobenzene and ethyl iodide, or by Friedel-Crafts' reaction from benzene and ethyl bromide. The industrial method uses benzene and ethylene at 100° under pressure. Chromic acid oxidises it to benzoic acid, but the isomeric xylenes to phthalic acids. Ethylbenzene is catalytically dehydrogenated to styrene, $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$, a material for synthetic rubber.

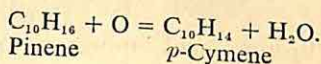
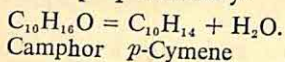
C_9H_{12} represents eight isomers *viz.* three trimethylbenzenes, three methylethylbenzenes, one propyl- and one iso-propylbenzene or cumene.

Mesitylene, sym. trimethylbenzene, $C_6H_3(CH_3)_3$, is formed by the dehydration of acetone with conc. H_2SO_4 (p. 139). It occurs in coal-tar in small quantities. It is a colourless, sweet-smelling liquid (b.p. 164.5°), volatile in steam. On oxidation with dilute HNO_3 , the methyl groups are successively converted into carboxyl groups, and finally, trimesic acid is formed:



These acids form *m*-xylene, toluene and benzene respectively on distillation with soda-lime. Mesitylene resembles the xylenes in its properties; its constitution follows from its synthesis from acetone (p. 139).

***p*-Cymene**, *p*-methylisopropylbenzene, $CH_3 \cdot C_6H_4 \cdot CH(CH_3)_2$, is present in some essential oils such as oil of cumín, oil of thyme and some eucalyptus oils. It is commercially obtained from oil of turpentine, and is also formed when camphor is dehydrated with phosphorus pentoxide. Pinene, the main constituent of turpentine oil, on heating with iodine or conc. H_2SO_4 , also gives *p*-cymene. It is a bye-product of spruce wood pulp industry.

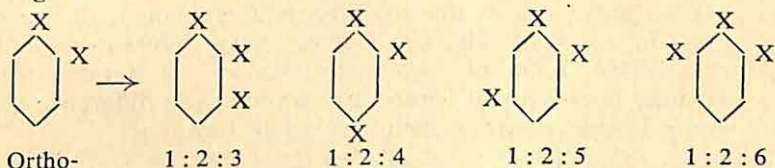


p-Cymene is a pleasant-smelling liquid (b.p. 175°) which, on oxidation, gives *p*-toluic and finally, terephthalic acid. This shows that two alkyl radicals are present in para-position. The structure of *p*-cymene, which follows from its synthesis, is $CH_3 \text{---} \text{C}_6\text{H}_4 \text{---} CH(CH_3)_2$. *m*-Cymene occurs in light resin oil and some terpenes.

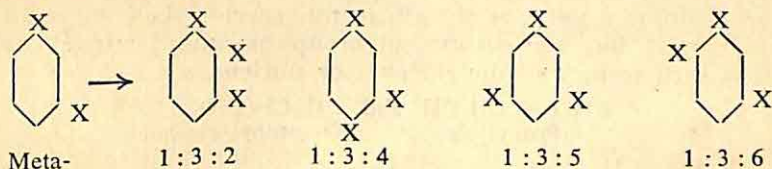
Orientation.—Benzene, as already mentioned, forms three di-substituted derivatives, *viz.*, *o*-, *m*- and *p*-; the isomerism is due to different positions occupied by the substituents. Determination of relative positions of groups or atoms in the nucleus is known as *orientation* (*orienté*, situated). This is done either by referring the compound to, or transforming it into, substances whose substituted positions are known, or by *Körner's absolute method of orientation* (1874). The first we have discussed in connection with the identification of xylenes (p. 333). Here we require some substances of known structure, which the unknown compound can be obtained from, or converted into. The assumption (which is generally, but not invariably, true) is made that substituents retain their relative positions during transformations. With so many organic compounds of known constitution, it is no problem to find a reference substance to-day, but the position was different at the early stages.

Körner's method is based on the fact that when a di-derivative is converted into a tri-substituted one by replacing another atom of

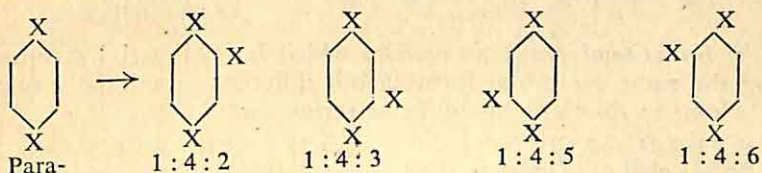
hydrogen (by a similar or dissimilar substituent), the number of such tri-derivatives is *different* in the three cases. The ortho-compound gives two-, the meta- yields three, and the para- only one tri-derivative. Hence from the number of these tri-derivatives, it is possible to identify the isomers. The ortho-di-derivative of benzene, $C_6H_4X_2$, can give the following tri-derivatives:



1:2:3 and 1:2:6 are identical as also 1:2:4 and 1:2:5. Hence it actually gives only *two* tri-derivatives. Similarly, the meta-compound can form the derivatives shown below, of which 1:3:4 and 1:3:6 are



identical. Hence it gives *three* tri-substituted derivatives. The four possible substitutions in the para-compound make one and the *same* tri-derivative.



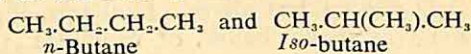
The rule also holds good if the new entrant is different from the substituents already present. Altogether we get six different tri-derivatives in this case, while if all the substituents are identical, we have only three.

Though Körner's method is theoretically conclusive, in actual practice all the tri-derivatives may not be possible to prepare directly, owing to the directing influence of the substituents already present (p. 330); the yield of some of them may be poor enough to escape detection. It is sometimes convenient to follow the converse of Körner's method, which is also true. Thus three diamino-benzenes (*o*-, *m*- and *p*-) are obtained by the removal of the carboxyl group on distilling the six diaminobenzoic acids, $C_6H_3(NH_2)_2COOH$, with soda-lime. The diaminobenzene from three is the meta-compound, that obtained from two is the ortho- whilst para-diaminobenzene results from only one diaminobenzoic acid.

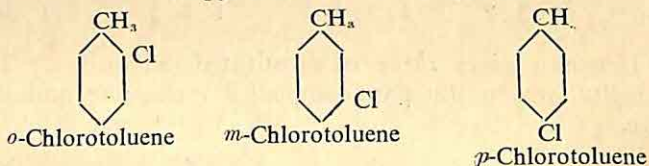
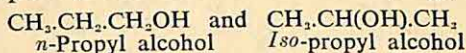
The same method is applicable to the orientation of tri-substituted derivatives as well. If the substituents are not different, the 1:2:3-compound gives two, 1:3:4 gives three, and 1:3:5 only one tetra-derivative. The reverse procedure may also be adopted, if necessary.

Isomerism.—Compounds which have the same molecular formula but differ at least in one physical or chemical property, are called isomers (p. 46). The crystalline forms of allocinnamic acid (q.v.) melting at 32° , 42° , 58° and 68° , which give identical solutions, are, however, regarded as polymorphic rather than isomeric. These consist of identical molecules packed into the crystal in four different ways. Isomerism, as we have seen, is due to different arrangement of the constituent atoms in the molecule, *i.e.*, isomers have different *structure* or *constitution*. This kind of isomerism, known as *simple structural isomerism*, may be sub-divided into three groups; the difference between such isomers is obvious from their structural formulas:

(i) *Nuclear* or *chain isomerism* which arises from a difference in the arrangement of the carbon atoms in the carbon chain, *e.g.*,



(ii) *Position isomerism* in which the carbon skeleton or nucleus remains intact but the substituent group or atom occupies different positions with respect to the skeleton or nucleus, *e.g.*,

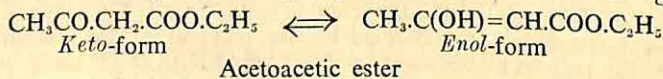


(iii) *Functional group isomerism* which is exhibited by compounds having the same molecular formula but different functional groups, *i.e.*, they belong to different homologous series, *e.g.*,



Metamerism (p. 123) stands for functional group isomerism within the same homologous series; *e.g.*, diethyl ether, $\text{C}_2\text{H}_5\text{O.C}_2\text{H}_5$, and methyl propyl ether, $\text{CH}_3\text{O.C}_3\text{H}_7$, are metameric.

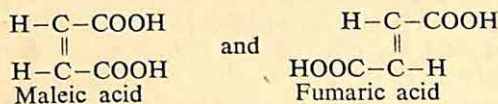
Tautomerism or *dynamic isomerism* (p. 198) is a special case of functional group isomerism. Here generally a hydrogen atom migrates from one carbon to another with a change in the distribution of valence bonds. Such change is usually rapid and also reversible, *e.g.*,



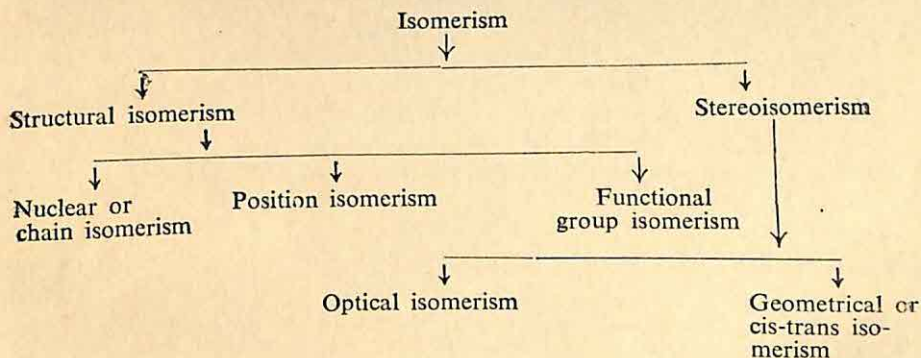
Isomerism is also possible amongst compounds having the same molecular formula, the same functional groups and also the same structure but a *different configuration*, *i.e.*, the isomers have different *three-dimensional space arrangement* of the atoms or groups within the molecule. This is called *stereoisomerism* or *space isomerism*, it may be exhibited in two ways:

(i) *Optical isomerism* (p. 191) which is exhibited by compounds having an asymmetric structure. The isomers have different action on polarised light but possess identical physical and chemical properties, e.g., the three lactic acids (*d*-, *l*- and *dl*-), $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$.

(ii) *Geometrical or cis-trans isomerism* (p. 250) which arises out of restricted rotation in the molecule due to a double bond to which are attached dissymmetric groups, or due to cyclic structures. In geometrical isomers, the atoms forming the molecule are similarly linked to one another but some of the atoms in one isomer lie further apart than the corresponding atoms in the other. In co-planar ring compounds such as benzene hexachloride, $\text{C}_6\text{H}_6\text{Cl}_6$, (p. 320) geometrical isomerism is possible because free rotation about cyclic single bonds is difficult or impossible owing to the strain involved therein, the structure being more or less rigid. The isomers have quite different properties (vide p. 249), and may be optically active if they contain asymmetric carbon atom and have no plane of symmetry e.g., cyclopropane-1:2-dicarboxylic acid occurs in *d*- and *l*-forms. Examples are



and also benzene hexachlorides and inositols (p. 313). More than one spatial representation is not possible in the case of acetylene derivatives such as $\text{R.C}\equiv\text{C.R}$ (in which the two tetrahedra are placed face to face). Such compounds are incapable of exhibiting cis-trans isomerism.



In the theory of chemical structure, it is implied that the different atoms in the molecule of an organic compound have an arrangement which is definite and unalterable; otherwise isomerism could not occur.

QUESTIONS

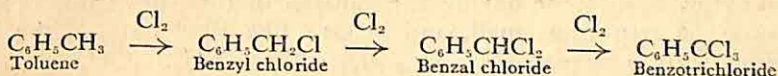
1. What do you understand by the term 'Orientation'? Explain with the aid of examples how this has been carried out in the case of di- and tri-substitution products of benzene. B.Sc. Degree Exam., 1942, Travancore Uni.

2. What are the common methods of preparation of aromatic hydrocarbons? Enumerate the reactions in which they differ from aliphatic ones.
 3. Explain one method of determining the positions of the substituents in the disubstitution products of benzene. B.Sc. London, 1923; B.Sc. 1947, Nagpur Uni.
 4. Give the different possible structures for the aromatic hydrocarbon C_8H_{10} . How can the correct configuration be determined?
 5. What evidence is there to justify the assumption that the six hydrogen atoms in benzene are equivalent? B.Sc., Pass, 1935, Calcutta Uni.
 6. You are given a sample of di-chloro-benzene. How would you find out whether it is an ortho-, meta- or a para-compound? B.Sc., Pass, 1933, Dacca Uni.
 7. In the preparation of a di-derivative of benzene from a mono-derivative, what factors determine the position to be taken up by the newly entering group? How would you proceed to determine the nature of a di-derivative of benzene? B.Sc. Pass, 1937, Dacca Uni.
 8. How would you proceed to determine the orientation of groups in the isomeric xylenes? Explain fully the principle involved.
 9. Write a short essay on the orienting effect of a group on aromatic substitution. B.Sc. (Principal Chemistry) 1941, Bombay Uni.; A. I. C. 1940.
 10. Describe the methods of orientation of disubstituted products of benzene. B.Sc. Pass, 1951, Rajasthan Uni.; B.Sc. Degree Exam., 1941, Madras Uni.
 11. Classify the various kinds of isomerism in organic chemistry, mentioning the special feature of each type. B.Sc. Pass, 1949, Lucknow Uni.; B.Sc., 1952, Agra Uni. and Nagpur Uni.
 12. Explain clearly tautomerism and give three examples with important evidence. B.Sc. Pass, Agra Uni. 1950.
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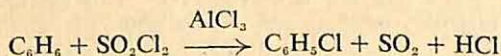
THE AROMATIC HALOGEN COMPOUNDS

Benzene forms, as already mentioned, both addition and substitution products with halogens. Additive compounds result when benzene, mixed with chlorine or bromine, is exposed to sunlight. Finally we get benzene hexachloride, $C_6H_6Cl_6$, or hexabromide, $C_6H_6Br_6$. These are unstable. Fluorine decomposes the hydrocarbon, and iodine reacts with it only in presence of an oxidising agent. In aromatic halogen-substituted compounds, the halogen may be (i) in the side-chain, or (ii) in the ring. The hydrogen in a side-chain may be replaced by chlorine (or bromine) by passing it into the boiling hydrocarbon preferably in sunlight. All the hydrogen of $-CH_3$ in toluene can thus be replaced; the products behave like alkyl halides. Proximity of the benzene ring, however, makes the chlorine in the side-chain more mobile.



Compounds with halogen in the nucleus are more important. They are called aryl halides. Unlike alkyl halides, they are usually made from aromatic hydrocarbons directly, and seldom from the corresponding hydroxy-compounds.

Preparation.—(i) One or more hydrogen atoms of the nucleus may be replaced by chlorine or bromine by treating benzene at ordinary temperature in presence of a catalyst such as Fe, I_2 , etc. called 'halogen carriers'. Iodine derivatives in good yield are obtained at high temperature and in presence of an oxidising agent such as iodic acid; mercuric oxide, nitric acid, etc.; these decompose the hydriodic acid formed (*cf.*, iodination of paraffins, p. 71). If the ring has already a substituent, the position taken by the halogen is determined by the substitution rule (p. 330). When sulphuryl chloride, SO_2Cl_2 , in presence of $AlCl_3$ is employed at room temperature, chlorine enters the nucleus of benzene and its homologues; in presence of hydrogen peroxide, however, it goes to the side-chain.



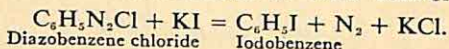
(ii) Hydroxybenzene (phenol) when treated with PCl_5 or PBr_5 gives chloro- or bromobenzene (*cf.*, formation of alkyl halides from alcohol, p. 71). The method is costly, and the yield poor due to formation of triphenyl phosphate, $(C_6H_5)_3PO$, mainly.



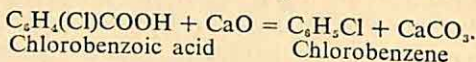
The hydroxyl in the side-chain may be replaced likewise:



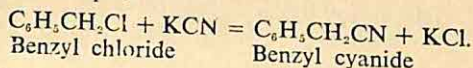
(iii) Diazobenzene salts (q.v.) readily yield halogenated benzenes on suitable treatment. Iodobenzene is thus conveniently obtained.



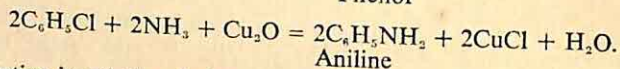
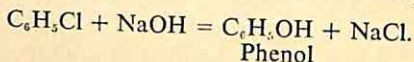
(iv) Halogenated acids, heated with soda-lime, give halogenated hydrocarbons; benzoic acid likewise gives benzene.



Properties.—The aryl halides are colourless liquids or solids which distil without decomposition. They are soluble in alcohol and ether but insoluble in, and heavier than, water; many are volatile in steam. The b.p. and sp. gr. of monohalogen derivatives of benzene (which are all liquids) gradually increase from fluoro- to iodo-benzene. Compounds with halogen in the nucleus differ considerably in their properties from those having the halogen in the side-chain. The latter possess an irritating smell, and behave like alkyl halides, the halogen being readily replaceable by -SH, -CN, -NH₂, -OH, etc., groups (pp. 74, 75). For example,

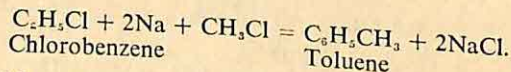


But the halogen in the ring is more firmly bound and cannot easily be replaced. Thus chlorobenzene gives phenol on heating with aqueous caustic soda under pressure at 300°, and forms aniline with ammonia at 200° under pressure in presence of cuprous oxide:



The relative inactivity of these aryl halides appears to be due to resonance involving unshared electrons of the halogen atom and the benzene ring, which shortens the C-halogen bond length (the C-Cl distance in chlorobenzene is 1.70A while that in alkyl chlorides is 1.76A) and increases the bond strength.

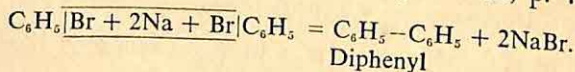
With sodium and alkyl halide it may be replaced by an alkyl group (*Wurtz-Fittig Reaction*).



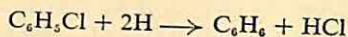
Aryl cyanides may be obtained by heating aryl bromides with anhydrous cuprous cyanide at about 200° in presence of pyridine.



An aryl halide in ether solution reacts with sodium to give diphenyl (*cf.*, formation of butane from ethyl iodide, p. 74).

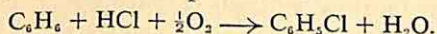


Aryl bromides and iodides but not chlorides form Grignard reagent such as phenyl magnesium bromide, C_6H_5MgBr , which behaves like alkyl magnesium halides and is of considerable synthetic value. Nickel-aluminium alloy in presence of caustic soda reduces an aryl halide to the parent hydrocarbon:



Preparation of chlorobenzene.—Benzene, mixed with a little iron powder, is taken in a flask fitted with a reflux condenser and an inlet tube for the passage of chlorine. It is heated to 60° on a water-bath and dry chlorine is passed into benzene until the increase in weight corresponds to the entrance of one Cl atom. The liquid is treated with dilute NaOH solution to remove the excess chlorine and HCl formed. It is dehydrated with $CaCl_2$ and fractionally distilled. The fraction coming between 130° – 135° is collected. Chlorobenzene is technically made in this way.

Chlorobenzene is also manufactured from benzene, air and hydrochloric acid by the Raschig process (p. 387). Oxidation of HCl by air in presence of $CuCl_2$ to chlorine, and chlorination of benzene by the liberated chlorine are combined in one step at 230° .



Chlorobenzene is a colourless heavy (sp. gr. 1.128) liquid (b.p. 132°) with a pleasant smell. It is insoluble in water, but soluble in ether and alcohol. With conc. H_2SO_4 , it gives *o*- and *p*-chlorosulphonic acid. And on nitration, it is converted into *o*- and *p*-nitrochlorobenzene. The chlorine in chlorobenzene is difficult to replace (p. 340). At about 40° in an inert atmosphere, sodium and chlorobenzene form phenylsodium, C_6H_5Na . Chlorobenzene is mostly used for making synthetic phenol, aniline and D.D.T. U.S.A. made 436 million lb. of it in 1955.

Bromobenzene, phenyl bromide, C_6H_5Br , is made similarly by adding, drop by drop, the required bromine (160 g) to benzene (78 g), containing a little iron powder (2 g) and purified by distillation. It can also be prepared by the general methods (pp. 339-40). Bromobenzene is a colourless, heavy (sp. gr. 1.49 at 20°) liquid (b.p. 155°), resembling chlorobenzene in its behaviour. It is, however, more reactive. Magnesium ribbon dissolves in ethereal solution of bromobenzene if everything is *absolutely dry*, and forms phenyl magnesium bromide or Grignard reagent.

Iodobenzene, phenyl iodide, C_6H_5I , may be obtained by heating in a sealed tube iodine, benzene and nitric acid. It is more easily prepared by warming an aqueous solution of diazobenzene chloride with potassium iodide, and purified by steam distillation (p. 340).

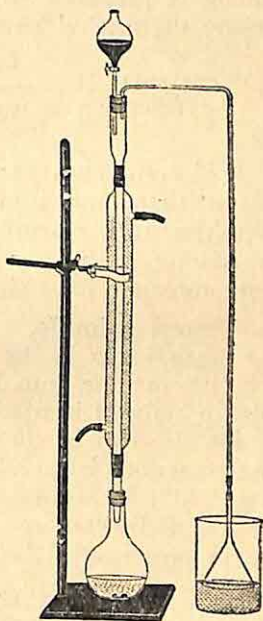
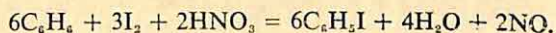


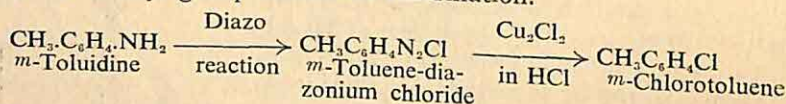
Fig. 53. Preparation of bromobenzene.

Iodobenzene is a colourless, heavy liquid (sp. gr. 1.861), boiling at 188°. It is more reactive than chloro- or bromo-benzene (*cf.*, reactivity of alkyl iodides, pp. 74, 75).

Iodobenzene, in cold chloroform solution, forms with dry chlorine yellow crystals of iodobenzene dichloride, $C_6H_5I \cdot Cl_2$. It gives iodosobenzene, $C_6H_5I \cdot O$, with dilute NaOH. Iodosobenzene suffers autoxidation, on steam distillation, giving iodoxybenzene, $C_6H_5IO_2$, and iodobenzene:

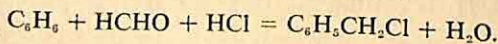
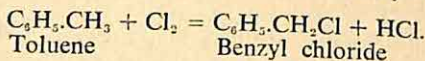


Chlorotoluenes, tolyl chlorides, $C_6H_4(CH_3)Cl$.—There are three isomeric chlorotoluenes (*o*-, *m*- and *p*-). The ortho- and para-compounds (but not the meta-) are obtained by the direct chlorination of *cold* toluene in presence of a halogen carrier; meta-chlorotoluene is prepared from meta-toluidine. Activation of the benzene ring by the methyl group facilitates chlorination.

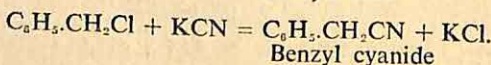
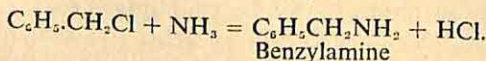
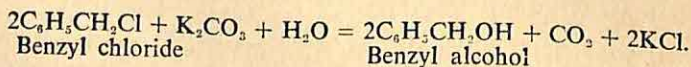


Chlorotoluenes are heavy, colourless and pleasant-smelling liquids heavier than, and immiscible with, water. In physical and chemical properties, they resemble chlorobenzenes. Potassium permanganate or dichromate readily oxidises them to corresponding chlorobenzoic acids. Bromotoluenes have similar properties.

Benzyl chloride, $C_6H_5 \cdot CH_2Cl$, isomeric with the chlorotoluenes, has the halogen in the side-chain. It is commercially made by passing *dry* chlorine gas into *boiling* toluene until the theoretical sp. gr. (or gain in weight) is reached. Unlike the direct chlorination of paraffins (*p.* 43), this can be controlled so as to obtain any of the three products. The reaction is accelerated by ultraviolet light. Benzyl chloride (b.p. 179°) is separated from the unchanged toluene (b.p. 110°) by fractional distillation. Benzene, formaldehyde and HCl react at about 80° in presence of $ZnCl_2$ or H_3PO_4 to form benzyl chloride.



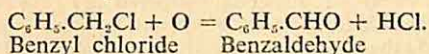
It is a colourless liquid with an unpleasant smell; the vapour attacks the eyes. It is insoluble in water, but dissolves in most organic solvents. Like an alkyl halide, benzyl chloride produces benzyl alcohol on hydrolysis, benzyl cyanide with potassium cyanide, benzylamine with ammonia, and so on (*cf.*, ethyl iodide, pp. 74, 75), but at a much faster rate (*cf.* chlorotoluenes).



Benzyl chloride forms with concentrated nitric acid isomeric nitrobenzyl chlorides, $C_6H_4(NO_2)CH_2Cl$, a hydrogen in the ring being substituted by a nitro group. It gives dibenzyl when heated with copper powder (*cf.* formation of ethane from methyl iodide, p. 44).

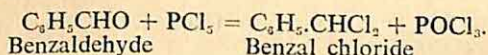


Alkaline pot. permanganate oxidises benzyl chloride to benzoic acid, $C_6H_5\cdot COOH$; it can, therefore, be distinguished from the isomeric chlorotoluenes which form chlorobenzoic acids, $C_6H_4(Cl)\cdot COOH$. Heated with cupric or lead nitrate, it is oxidised to benzaldehyde:



Benzyl chloride is chiefly employed for making benzyl alcohol. Benzyl bromide has similar properties; it was used as a 'poison gas' in the war of 1914-18.

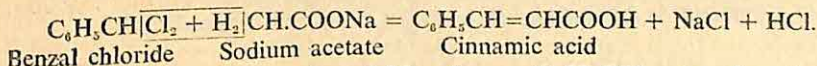
Benzal chloride, benzylidene chloride, $C_6H_5\cdot CHCl_2$, may be prepared by the action of PCl_5 on benzaldehyde (*cf.* formation of ethylidene chloride from acetaldehyde, p. 129). It is manufactured by passing dry chlorine into boiling toluene until the required increase in weight is attained.



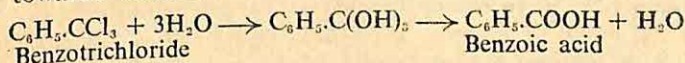
Benzal chloride is a colourless liquid (b.p. 206°) behaving as an alkylene halide (with two halogen atoms linked to the same C atom) and as an aromatic compound. Like benzyl chloride it provokes tears. It is hydrolysed by milk of lime to benzaldehyde. Benzaldehyde is thus commercially made.



Heated with sodium acetate, benzal chloride forms cinnamic acid:



Benzotrichloride, phenylchloroform, $C_6H_5\cdot CCl_3$, is the final product of chlorination of boiling toluene; chlorine is passed until there is no further increase in weight. Benzotrichloride boils at 213° , and on hydrolysis with milk of lime or steam under pressure, readily gives benzoic acid (*cf.* hydrolysis of chloroform, p. 79). It is a commercial method. Close proximity of the benzene ring to the methyl carbon atom facilitates the removal of chlorine (p. 339); chloroform is rather resistant towards alkalis.

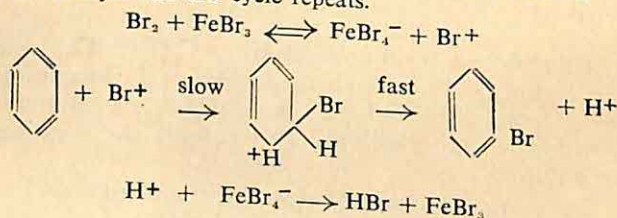


***o*-Dichlorobenzene**, $C_6H_4Cl_2$, (b.p. 179°) is a useful contact insecticide; mixed with glue, it protects cabinet work against wood-boring insects. It readily dissolves oxides of non-ferrous metals and is employed in cleaning copper and nickel articles. ***p*-Dichlorobenzene** (m.p. 56°) is a moth repellent for woollens. It is also a fumigant, germicide and deodorant. Chlorobenzene,

on further chlorination, gives *o*- and *p*-dichlorobenzene which are also obtained as bye-products in the manufacture of chlorobenzene.

***pp'*-Dichloro-diphenyl-trichloroethane** or **D.D.T.**, $\text{CCl}_3\text{-CH}(\text{C}_6\text{H}_4\text{Cl})_2$, is a very powerful insecticide (made by condensing chlorobenzene and chloral at about 30° in presence of H_2SO_4) practically odourless and remarkably persistent. It was extensively used during the last war for controlling typhus and malaria fever by killing lice and mosquitoes respectively. But insects can develop resistance to it. A bed sprayed with D.D.T. remains fatal to lice even after 6-8 laundings. The compound was first prepared by Zeidler in 1874; Müller in 1939 showed it to be an insecticide.

Mechanism of substitution.—Formation of bromobenzene was formerly explained by the addition-elimination theory which assumed a bromine molecule to add to a double bond in benzene followed by the elimination of HBr . This has proved untenable and been replaced by the ionic mechanism. The catalyst e.g., Fe and the halogen, say bromine, form FeBr_3 which with a bromine molecule gives a bromonium ion, Br^+ , and FeBr_4^- . Electrophilic Br^+ attacks one of the double bonds of benzene and yields a carbonium ion. A proton is now eliminated and the aromatic ring restored. The proton regenerates the catalyst and the cycle repeats.



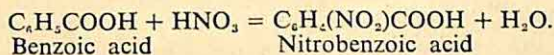
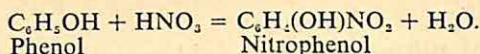
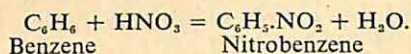
QUESTIONS

1. What important differences are exhibited by substitutions of a halogen atom in the side-chain and in the nucleus of an aromatic hydrocarbon?
2. Name the isomers having the formula $\text{C}_7\text{H}_7\text{Br}$. How would you distinguish them?
3. Explain the behaviour of chlorine towards the following hydrocarbons: (i) methane, (ii) acetylene, (iii) benzene and (iv) xylene. State the conditions under which reactions occur in each case.
4. "Experimental conditions are often a factor in determining the nature of products of a reaction." Illustrate this with reference to the reactions between (i) chlorine and toluene, (ii) sulphuric acid and ethyl alcohol.
5. Starting from benzene, how would you prepare (i) benzoic acid (ii) *p*-chloro-benzoic acid, (iii) benzaldehyde and (iv) *o*-nitro-benzyl bromide?
6. What substances are formed by the action of chlorine on (a) toluene in presence of a halogen carrier, and (b) boiling toluene? How would you distinguish the products obtained from the two reactions?
B.Sc. Pass, 1938. Dacca Uni.
7. Discuss in detail the products obtained by the reaction of chlorine and toluene, and indicate their industrial importance.
B.A. & B.Sc. Pass, 1938, Bombay Uni.
8. How are the chlorotoluenes prepared? Explain the method by which the orientation of a given chlorotoluene may be determined.
B.Sc. Degree Exam. 1941, Annamalai Uni.
9. How is iodobenzene prepared? Compare and contrast the properties of iodobenzene with those of ethyl iodide.
B.A. Degree Exam. 1942, Madras Uni.
10. A compound *A* contains 66.4% C, 5.5% H, and 28.1% Cl and gives, on continued boiling with dilute HNO_3 , *B* with 53.7% C, 3.2% H and 22.7% Cl. What are *A* and *B*? *Ans.* $\text{C}_6\text{H}_4(\text{CH}_3)\text{Cl}$, $\text{C}_6\text{H}_4(\text{COOH})\text{Cl}$.

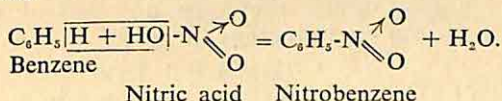
CHAPTER XXXIV

THE AROMATIC NITRO-COMPOUNDS

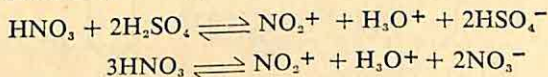
In contrast with the aliphatic, aromatic compounds directly form nitro-derivatives with conc. HNO_3 (p. 315). Benzene and nitric acid produce nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$, a hydrogen atom of the ring being replaced by a $-\text{NO}_2$ group. Other aromatic compounds such as phenols, acids, amines, aldehydes, etc., behave similarly. The nitro group, as a rule, enters the ring, and not the saturated side-chain which has, in some cases, a tendency to be oxidised by the acid. Aryl halides e.g., chlorobenzene *do not* form nitrobenzene with silver nitrite (cf., formation of nitroparaffins, p. 173). Boron trifluoride, BF_3 , improves the yield of aromatic nitro-compounds as a catalyst. Chloromycetin, an antibiotic, is so far the only naturally occurring aromatic nitro-compound.



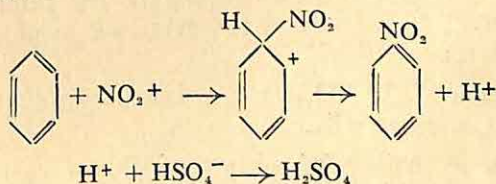
For nitration, conc. nitric acid (sp. gr. 1.5), fuming nitric acid or more usually a mixture of conc. HNO_3 and H_2SO_4 is employed. With dilute HNO_3 , nitration is not generally possible, presumably due to ionisation of the acid and consequent absence of $-\text{OH}$ group (of nitric acid) which is essential for the formation of water.



H_2SO_4 does not merely remove the water formed (thereby preventing undue dilution of HNO_3) for P_2O_5 cannot speed up the reaction like H_2SO_4 . It is now believed that the nitronium ion, NO_2^+ , set free by H_2SO_4 from HNO_3 or by conc. aqueous HNO_3 itself, is the nitrating agent (the existence of NO_2^+ has been shown by spectroscopic analysis and otherwise):



and the nitration proceeds as

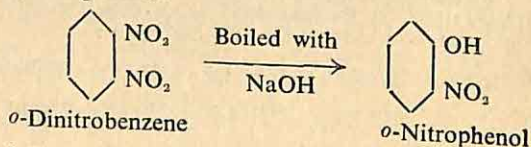


If nitration is done in H_2SO_4 solution, KNO_3 (or NaNO_3) may be employed instead of HNO_3 . Acetyl nitrate, $\text{CH}_3\text{CO.ONO}_2$, is a convenient nitrating agent for aromatic compounds; no water is formed during the reaction. It is, however, not quite stable and may explode on heating. It gives larger amounts of the ortho-isomer while HNO_3 yields more of the para-

The number of nitro-groups entering the benzene nucleus depends upon the nature of the compound, the concentration of nitric acid, and the temperature of the reaction. Generally, in the cold or at room temperature, a mononitro-derivative is formed, but with more concentrated acid, and at higher temperature, di- and tri-nitro-derivatives may be obtained. The nitro group deactivates the benzene ring, making the entry of the second nitro group rather difficult. Not more than three nitro groups can usually be introduced into benzene or its derivatives. Nitration proceeds smoothly if $-\text{CH}_3$, $-\text{OH}$, $-\text{NH}_2$, etc. groups are present in the ring to activate it; toluene, phenol, aniline, etc., are more readily nitrated than benzene. Phenol, for example, can be nitrated with *dilute* HNO_3 . A substituent in the ring has a directing influence on the entering $-\text{NO}_2$ group (p. 330). Oxidation of aromatic aldehydes during nitration with HNO_3 is not appreciable at about 0° .

If toluene or ethylbenzene is heated above 100° with dilute HNO_3 (d. 1.076) in a sealed tube, phenylnitromethane, $\text{C}_6\text{H}_5\text{CH}_2\text{NO}_2$, or phenylnitroethane, $\text{C}_6\text{H}_5\text{CH}(\text{NO}_2)\text{CH}_3$, is formed, the nitro group entering the side-chain.

Properties of nitro-compounds.—Most aromatic nitro-compounds are yellow, crystalline solids; a few *e.g.*, nitrobenzene are pale yellow liquids. They are soluble in common organic solvents such as alcohol, benzene, ether, etc., but insoluble in water. The mononitro-derivatives distil unchanged, but the di- and tri-nitro-compounds usually decompose on heating, sometimes with explosion. The majority of them are volatile in steam. In certain respects, however, they behave like aliphatic nitro-compounds. For example, they are not hydrolysed by caustic alkalis; they form amines on reduction in acid solution, etc. Aromatic nitro-compounds which are tertiary, do not form salts with alkalis (p. 174) or react with HNO_2 (p. 96). The nitro group in mono-derivatives is firmly attached to the nucleus and quite difficult to substitute. In di- and poly-nitro-derivatives or halogen-substituted nitro-compounds, however, it can be replaced:



Commercially, the nitro-compounds are important; some *e.g.*, trinitrotoluene (T.N.T.) and picric acid, are explosives; others form dye intermediates.

Nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$, is the simplest aromatic nitro-compound and important commercially.

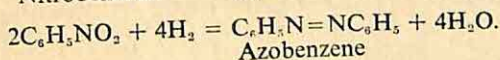
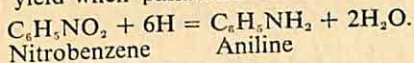
Preparation.—A well-cooled mixture of 50 c.c. of conc. HNO_3 (sp. gr. 1.4) and 60 c.c. of conc. H_2SO_4 is slowly added to 45 c.c. of benzene taken in a flask. It is shaken and cooled, if required, to keep the temperature below 50° (to avoid the formation of *m*-nitrobenzene). The mixture is heated under reflux on water-bath to about 70° for 45 minutes with occasional shaking. The cooled liquid is poured into water (about 400 c.c.); the oily, heavy, insoluble nitrobenzene is removed and washed in a separating funnel with water and then

with a dilute solution of Na_2CO_3 to remove the free acid. It is again washed with water, dehydrated with fused CaCl_2 , and distilled with an air-condenser. The fraction coming between 207° - 211° is collected. It is dangerous to distil to dryness or raise the temperature above 214° ; an explosion may occur due to higher nitro-compounds.

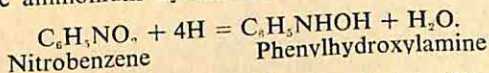
The industrial process is similar; the nitration is carried out in large, cast iron pans fitted with a stirrer and kept cool by circulating water. The temperature is finally raised to 80° by external steam to complete the reaction which takes 3-4 hours. The liquid is cooled and transferred to a tank with a conical base. The heavier acid layer is drawn off and used again. Nitrobenzene is washed with water or dilute alkali and purified by distillation, if necessary. Excess of acid gives *m*-dinitrobenzene.

Properties.—Nitrobenzene is a pale yellow, oily liquid (sp. gr. 1.204 at 20°), boiling at 209° . It smells somewhat like oil of bitter almonds; it is called artificial oil of bitter almonds and used for scenting cheap soap and boot-polish. Commercially, nitrobenzene is known as *essence* or *oil of mirbane*. It is very stable, being unaffected by acids, alkalis or oxidising agents. It forms *o*- and *p*-nitrophenols on heating with solid KOH. Nitrobenzene may be reduced, in acid solution, to aminobenzene or aniline, for making which it is chiefly employed. It is volatile in steam and is purified by steam distillation (p. 8). Nitrobenzene is a poison, it is readily absorbed through the skin and destroys red blood corpuscles. It is a good solvent and an oxidising agent. On reduction, nitrobenzene yields various products depending on the reducing agents and its pH.

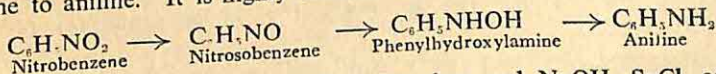
(i) Reduced in strongly *acid* solution e.g., with SnCl_2 and HCl, or zinc and HCl, nitrobenzene forms aniline. Aromatic nitro-compounds, as a rule, are reduced to amino-compounds by acid reducing agents. On hydrogenation, nitrobenzene gives aniline in presence of platinum or Raney nickel but azobenzene in 100% yield when palladium on CaCO_3 support is employed.



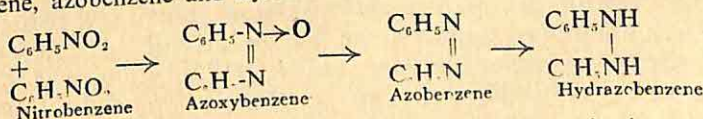
(ii) By *neutral* reducing agents such as aluminium-mercury couple or zinc dust and aqueous NH_4Cl , nitrobenzene is mainly reduced to phenylhydroxylamine. Alcoholic ammonium hydrosulphide acts likewise in the cold.



Phenylhydroxylamine is an intermediate product in the reduction of nitrobenzene to aniline. It is highly reactive and readily forms aniline:

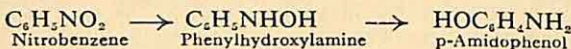


(iii) *Alkaline* reducing agents like zinc dust and NaOH, SnCl_2 and NaOH, sodium methoxide in alcohol, etc. convert nitrobenzene successively into azoxybenzene, azobenzene and hydrazobenzene:

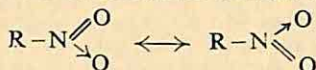


(iv) By electrolytic reduction in strongly acid solution, nitrobenzene yields *p*-amidophenol, an important dye intermediate; phenylhydroxylamine is probably

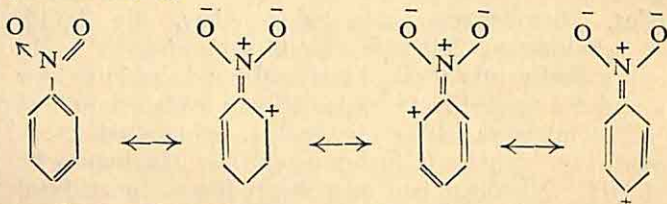
an intermediate product. In weakly acid solution, however, aniline is the main product.



There is evidence to show that the oxygen atoms are equivalent in the nitro group which is stabilised by resonance between structures :

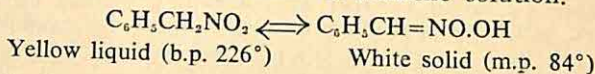


In nitrobenzene, however, resonance with the ring occurs and additional structures are possible such as

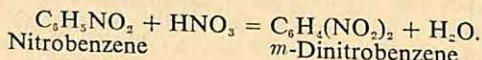


in which oxygen atoms carry negative charges; the corresponding positive charges are on the nitrogen atom and on either *o*- or *p*-carbon in the benzene ring.

Phenylnitromethane, $\text{C}_6\text{H}_5\text{CH}_2\text{NO}_2$, isomeric with nitrotoluenes, is obtained by heating benzyl iodide, $\text{C}_6\text{H}_5\text{CH}_2\text{I}$, with silver nitrite in aqueous alcohol, or toluene with dilute HNO_3 in a sealed tube above 100° . It is a yellow liquid, behaving like a primary nitroparaffin. It exists in two tautomeric forms, the ordinary nitro-form is stable; HCl precipitates the aci-form from its alkaline solution.



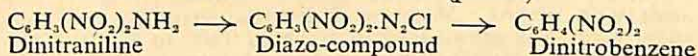
***m*-Dinitrobenzene**, $\text{C}_6\text{H}_4(\text{NO}_2)_2$, is made by treating nitrobenzene with a mixture of equal amounts of conc. H_2SO_4 and fuming HNO_3 (sp. gr. 1.5); *o*- and *p*-dinitrobenzenes are also simultaneously formed (about 8%).



Nitrobenzene (1 part) is slowly added with shaking to the acid mixture (3 parts) and heated on boiling water-bath for about an hour. On pouring the hot liquid with stirring into cold water, *m*-dinitrobenzene solidifies. It is filtered, washed with water and recrystallised from alcohol. The *o*- and *p*-compounds formed, remain in solution in alcohol. The *o*- and *p*- are replaced by conc. HNO_3 (sp. gr. 1.42) if a larger proportion (1 : 3) of conc. H_2SO_4 is used.

m-Dinitrobenzene forms very pale yellow needles (m.p. 90°), insoluble in water but readily soluble in alcohol and ether. It is volatile in steam. It is used for making explosives, and mixed with other explosives, e.g., T.N.T. for lowering their melting points. On reduction with alcoholic ammonium sulphide, we get *m*-nitraniline, $\text{C}_6\text{H}_4(\text{NO}_2)\text{NH}_2$, and finally, *m*-phenylenediamine, $\text{C}_6\text{H}_4(\text{NH}_2)_2$. Tin and HCl give directly *m*-phenylenediamine, an important dyestuff intermediate. Alkaline pot. ferricyanide oxidises *m*-dinitrobenzene to mainly 2:4-dinitrophenol.

o- and *p*-dinitrobenzene are prepared from the corresponding dinitranilines by diazo-reaction followed by reduction of the diazo-compound with alkaline stannous chloride (p. 367).

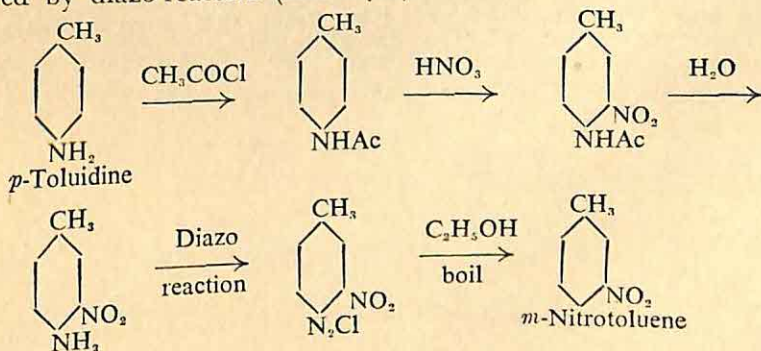


o- and *p*-dinitrobenzene are colourless crystals melting at 118° and 173° respectively. Towards reducing agents, they behave like their meta-isomer. *o*- and *p*-dinitrobenzene, however, form *o*- and *p*-nitrophenol on boiling with caustic soda, and give *o*- and *p*-nitraniline with alcoholic ammonia (distinction from the *m*-isomer). The *m*-compound can thus be separated from *o*- and *p*- with boiling caustic soda solution.

5-Trinitrobenzene, $\text{C}_6\text{H}_3(\text{NO}_2)_3$ (1:3:5), the most important of the three trinitrobenzenes, is produced by heating *m*-dinitrobenzene for about 5 days with a mixture of fuming HNO_3 and conc. H_2SO_4 . It is rather difficult to introduce the third nitro group into the benzene ring. Trinitrobenzene crystallises in colourless plates (m.p. 122°). It is used in making explosives, and as an indicator for titrating weak acids (it gives a deep yellow colour with alkalis). Heated with sodium methoxide in methanol, it forms 3:5-dinitroanisole, $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{OCH}_3$.

Nitrotoluenes, $\text{C}_6\text{H}_4(\text{CH}_3)\text{NO}_2$, are important for their ready conversion into the corresponding toluidines required for making dyestuffs. *o*- and *p*-nitrotoluene (with very little of the *m*-isomer) are obtained by the direct nitration of toluene. With acetyl nitrate, toluene gives about 90% of *o*-nitrotoluene. The *o*-compound melts at -4° and the para- at 54° . Hence they may be separated by freezing, or by fractional distillation under reduced pressure. *o*-Nitrotoluene is a perfume; both are employed in the dye industry. Mononitrotoluenes are isomeric with phenylnitromethane, $\text{C}_6\text{H}_5\text{CH}_2\text{NO}_2$, from which they can be distinguished by oxidation. *o*-Nitrotoluene forms *o*-aminobenzoic acid, $\text{C}_6\text{H}_4(\text{NH}_2)\text{COOH}$, on heating with alcoholic caustic soda by 'internal oxidation'.

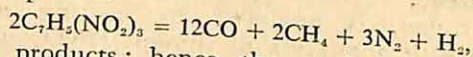
***m*-Nitrotoluene**, a liquid (b.p. 230°), is prepared indirectly from *p*-toluidine, $\text{C}_6\text{H}_4(\text{NH}_2)\text{CH}_3$. The amino group is protected by acetylation and the acetyl compound is nitrated. The amino group is removed by diazo-reaction (*vide infra*).



2:4:6-Trinitrotoluene is one of the most important explosives, briefly termed T.N.T. or *Trotyl*.

It is made by dropping toluene into a mixture of nitric and fuming sulphuric acids with stirring. Mono- and di-nitrotoluenes formed are separated from the spent acids and nitrated again at about 110° to T.N.T. The product is poured into water and crystallised from alcohol, or treated with Na_2SO_3 to free it from isomerides derived from *m*-nitrotoluene (about 5% of the latter is formed during nitration of toluene).

Trinitrotoluene is a pale yellow, crystalline solid melting at 81° without decomposition. It is toxic and explodes only on detonation or when burnt in large quantities; mercury fulminate is a common detonator. *Ammonal* (or *amatol*), a high explosive, is a mixture of T.N.T. and ammonium nitrate (in varying proportions). T.N.T. is used for the filling of torpedoes, shells and bombs. On explosion, it is believed to decompose as



giving gaseous products; hence the explosive violence (cf., nitroglycerine, p. 116). The molecule itself supplies the oxygen necessary for combustion. The explosive violence of the first hydrogen-bomb was equivalent to that of about 14 million tons of T.N.T.

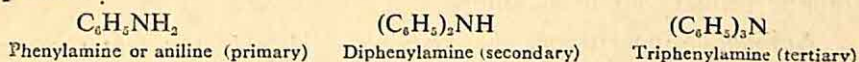
QUESTIONS

- How would you prepare from benzene the following compounds :
(a) benzoic acid, (b) benzyl chloride, (c) aniline, (d) chlorobenzene?
B.A. Pass, 1938, Bombay Uni.
- Give an account of the method of preparing and purifying nitrobenzene and describe its properties. To what uses has it been put?
B.Sc. Pass, 1936, Dacca Uni.
- Give an account of the reactions which occur when nitrobenzene is reduced under different experimental conditions.
A.I.C., 1940.
- In what respects do the aromatic nitro-compounds differ from the nitro-paraffins?
- By what chemical reactions would you distinguish between any three of the following pairs of substances? (a) nitroethane and nitrobenzene, (b) ethyl cyanide and ethyl isocyanide, (c) aldohexose and ketohexose, (d) benzyl chloride and *p*-chlorotoluene.
B.Sc. 1942, Agra Uni.
- Describe the preparation of nitrobenzene in the laboratory. How can the following compounds be prepared from it? (a) aniline, (b) phenol, (c) iodobenzene.
B.A. & B.Sc. Degree Exam., 1942, Andhra Uni.
- Give a detailed description of the products of reduction of nitrobenzene under different conditions. B.Sc. Exam. 1945, Benares Hindu Uni.; B.Sc. Pass, 1952, Allahabad Uni. & Rajasthan Uni.

CHAPTER XXXV

THE AROMATIC AMINO-COMPOUNDS

The aromatic amines, like the aliphatic, may be looked upon as theoretically derived from ammonia, NH_3 , by the replacement of hydrogen by aryl groups. They are primary, secondary or tertiary according as one, two or all the hydrogen atoms of ammonia are thus replaced:

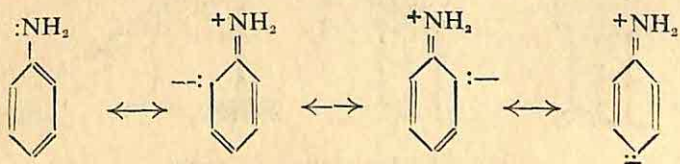


Secondary and tertiary amines may have both alkyl and aryl groups *e.g.*, phenylmethylaniline, $\text{C}_6\text{H}_5\text{NHCH}_3$, and phenyldimethylamine, $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$. The primary aromatic amines may also be regarded as derivatives of aromatic hydrocarbons, formed by the substitution of nuclear hydrogen atoms by amino groups. Thus $\text{C}_6\text{H}_5\text{NH}_2$ is aminobenzene, $\text{C}_6\text{H}_4(\text{CH}_3)\text{NH}_2$ is aminotoluene and $\text{C}_6\text{H}_4(\text{NH}_2)_2$ is diaminobenzene. The $-\text{NH}_2$ group may be in the side-chain, *e.g.*, benzylamine, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$. It behaves like aliphatic amines (*cf.*, benzyl chloride, p. 342).

The aromatic amines differ from the aliphatic in their mode of formation and, to some extent, in their chemical behaviour. They are, as a rule, obtained by the reduction of corresponding nitro-compounds. Due to the phenyl group, aromatic amines are much weaker bases than ammonia or aliphatic amines. At 25°K for ammonia is 1.75×10^{-5} , for aniline, $\text{C}_6\text{H}_5\text{NH}_2$, 4.6×10^{-10} and for *n*-hexylamine, $\text{C}_6\text{H}_{13}\text{NH}_2$, 5.0×10^{-4} . The basic character weakens gradually with increasing number of phenyl groups. Diphenylamine ($k = 7.6 \times 10^{-14}$) is weaker than aniline, and triphenylamine has no basic property at all.

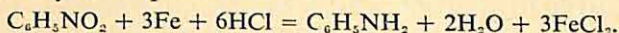
H

The lone pair of electrons on nitrogen in amines, $\text{R}:\ddot{\text{N}}:\text{H}$, are available for forming a coordinate bond with a proton; so amines behave as *proton acceptors* or bases. Any group that pulls these electrons away from the nitrogen would, therefore, weaken the base. Resonance of the unshared pair of electrons on nitrogen with the unsaturated electrons on the benzene ring of aniline (this is not possible in aliphatic amines) makes the lone pair less available for bonding with a proton. Furthermore, a small positive charge on nitrogen tends to repel a proton; hence aniline is a weaker base than ammonia or methylamine.

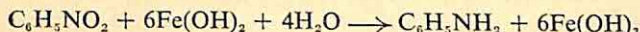
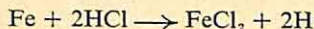


Steam from the can B (fitted with a safety tube to prevent excess pressure or back-rush), is led into the round-bottomed flask F containing the mixture of aniline, water, etc. The flask is connected to a condenser and heated on a sand-bath to prevent the condensation of steam coming from the can. Condensed steam and aniline collect in the receiver R. The distillation is continued till the distillate is no longer turbid. Powdered common salt (30 g.) is added to the distillate; practically all the aniline separates on shaking. It is extracted with ether and dehydrated with coarsely powdered KOH (aniline forms an addition compound with CaCl_2). Ether is removed by distillation on a boiling water-bath (with no flame nearby) and aniline is finally purified by distillation.

Commercially, nitrobenzene is reduced in cast iron cylinders fitted with mechanical stirrers with iron filing or powder (in place of more costly tin), water and about 1/40th of the hydrochloric acid theoretically required by the equation:

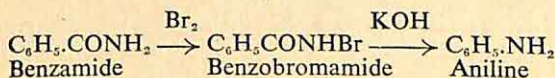


The mechanism of the reaction is not well established. One explanation is

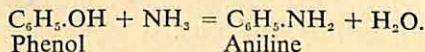


A little HCl is added to start the reaction, the regenerated HCl takes part in the reaction. Iron is finally obtained as black oxide, Fe_3O_4 , used as a pigment. Steam is blown into the vessel and the contents kept in agitation by the stirrer. Heat of reaction completes the process. Lime is added to neutralise the acid and decompose aniline hydrochloride. Aniline is separated by distillation in steam. Nitric acid is, however, costly for making nitrobenzene from benzene (*vide* method 4).

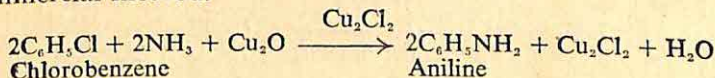
(2) Aniline may be obtained by Hofmann's reaction (p. 203) by treating the amide of benzoic acid with bromine and caustic potash. Other acid amides behave similarly.



(3) Phenol, when heated with the double compound of zinc chloride and ammonia to about 300° , yields aniline. Some secondary amine, $(\text{C}_6\text{H}_5)_2\text{NH}$, is also formed.



(4) Chlorobenzene (obtained by chlorinating benzene) and aqueous ammonia (28%) react under 60 atmos. pressure at about 200° in presence of cuprous oxide and chloride to form aniline. Cu_2Cl_2 acts as a catalyst. The conversion is nearly 90% under suitable conditions. About 1% diphenylamine and 5% phenol also result; these are easily removed. It is a commercial method.



(5) Aniline, in good yield, is obtained when nitrobenzene is reduced electrolytically in *weakly* acid solution; in strongly acid solution, *p*-amidophenol is formed (p. 348). Catalytic reduction of nitrobenzene gives aniline at room temperature if Raney nickel or platinum is used.

(6) Benzene and ammonia combine at 500° in presence of finely divided nickel to give aniline; the yield is, however, too poor.

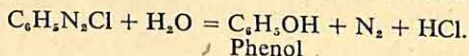
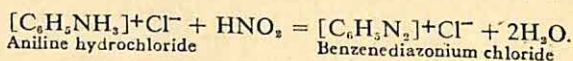


Other aromatic primary amines may be obtained similarly.

Properties.—Freshly distilled aniline is a colourless, oily liquid (b.p. 183°) with a characteristic (but not ammoniacal) smell. On exposure to light and air, it slowly turns deep brown due to oxidation of thiophene (present in coal-tar benzene used for making aniline). Aniline from synthetic benzene remains colourless. Aniline is slightly heavier than water (sp. gr. 1.024 at 16°) and is slightly soluble (about 3%) in it. Alcohol, ether or benzene dissolves it readily. Aniline is highly toxic but its toxicity is reduced on sulphonation and also its basicity; sulphanilic acid is almost non-toxic. It forms a yellow platinum-chloride, $(\text{C}_6\text{H}_5\text{NH}_2)_2 \cdot \text{H}_2\text{PtCl}_6$, with platinum chloride and HCl like aliphatic amines.

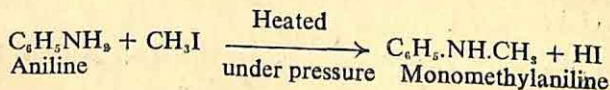
Aniline is a very weak base, almost neutral to litmus, but it forms with acids crystalline salts such as aniline hydrochloride or phenyl ammonium chloride, $[\text{C}_6\text{H}_5\text{NH}_3]^+ \text{Cl}^-$ (commercially known as 'aniline salt'), aniline sulphate, $[(\text{C}_6\text{H}_5\text{NH}_3)_2]^{++} \text{SO}_4^{--}$ etc., which give a strongly acid solution in water due to hydrolysis. Aqueous solution of aniline precipitates salts of Al, Fe and Zn as hydroxides.

Reactions.—(1) With nitrous acid *in the cold*, aniline salts produce diazonium salts which, on prolonged standing, or warming in aqueous solution, form phenol.

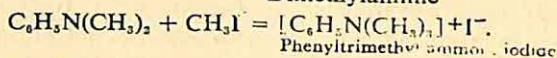
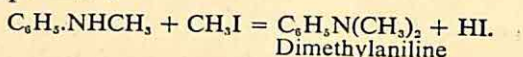


Aliphatic primary amines give alcohols, nitrogen and water with nitrous acid (p. 204) but no diazo-salt. Aliphatic diazo-salts, being extremely unstable, possibly split up into alcohols, etc. as soon as formed. Primary aromatic amines may be estimated by titration in acid solution with sodium nitrite using starch-iodide paper as indicator.

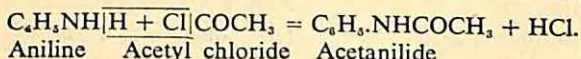
(2) Alkyl iodides replace the amino-hydrogen by an alkyl group in aromatic primary amines; secondary amines are first formed (cf., formation of aliphatic amines, p. 206).



Further substitution gives tertiary amines as well as quaternary ammonium compounds :

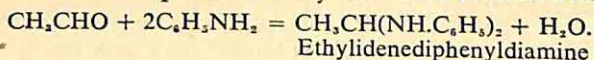


(3) With acid chlorides and anhydrides, aniline forms substituted amides, called *anilides*, which resemble aliphatic acid amides. These are crystalline and useful in the identification of amino compounds.

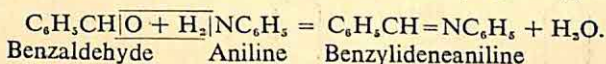


(4) Aniline and in fact, all primary amines, aliphatic or aromatic, give carbylamine or isocyanide reaction with chloroform and alcoholic caustic potash (p. 79).

(5) Aniline and aliphatic aldehydes form condensation products :



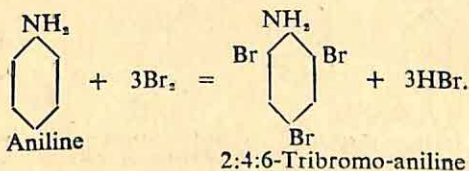
With benzaldehyde, however, only one molecule of aniline reacts on heating on water-bath to produce benzylideneaniline (m.p. 48°), a *Schiff's base*.



(6) Similarly, on boiling aniline with carbon disulphide in presence of powdered caustic potash, thio-carbanilide, a derivative of thio-urea, results. It forms colourless plates (m.p. 154°) and is an accelerator in the vulcanisation of rubber.



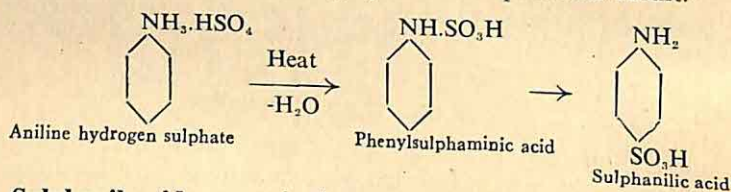
(7) With chlorine or bromine, aniline reacts much more readily than benzene, forming trichloro- or tribromo-aniline; the benzene ring is activated by the amino-group. In chlorination, a water-free solvent e.g., chloroform is used to avoid oxidation of aniline. Iodine, however, forms *p*-iodo-aniline; hydriodic acid formed combines with the product to yield a salt, $\text{C}_6\text{H}_4\text{INH}_2\cdot\text{HI}$. Sodium bicarbonate solution may be added to fix up the acid. The reaction with bromine-water is quantitative and used for the estimation of aniline. If aniline is first acetylated to acetanilide (thus reducing the activating effect of the amino group) and then brominated, *o*- and mostly *p*-bromo-derivatives result, which on hydrolysis give *o*- and *p*-bromoaniline. *p*-Chloroaniline, $\text{Cl}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$, results on heating *p*-chlorobromobenzene, $\text{Cl}\cdot\text{C}_6\text{H}_4\cdot\text{Br}$, with ammonia and cuprous oxide.



(8) Aniline undergoes oxidation readily, and different products, depending on the condition and oxidising agent, are formed:

Oxidising agent	Product
Alkaline pot. permanganate	Azobenzene, $C_6H_5-N=N-C_6H_5$
Neutral pot. permanganate	Azobenzene and nitrobenzene
Acid pot. permanganate	Aniline black (a valuable dyestuff)
Chromic acid	<i>p</i> -Benzoquinone, $C_6H_4O_2$
Hypochlorous acid	<i>p</i> -Amidophenol, $C_6H_4(OH)NH_2$
Conc. nitric acid	Aniline decomposes
Monopersulphuric acid (Caro's acid)	Nitrosobenzene, C_6H_5NO , and nitrobenzene, $C_6H_5NO_2$

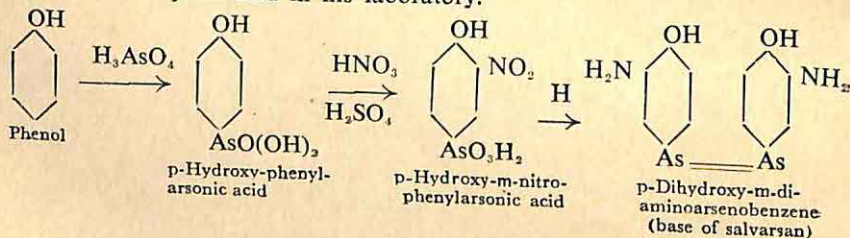
(9) Aniline sulphate, $(C_6H_5NH_3)_2SO_4$, (made by adding H_2SO_4 to aniline) on heating to $180-200^\circ$ with fuming H_2SO_4 , undergoes an *intra-molecular change* and yields *p*-aminobenzenesulphonic acid or sulphanilic acid—a little of the *o*-compound is also formed. Phenylsulphaminic acid is probably an intermediate product. Traces of iron salts promote oxidation and highly coloured products result.



Sulphanilamide, *p*-aminobenzenesulphonamide, $NH_2C_6H_4SO_2NH_2$ (m.p. 163°), is the nucleus essential for the streptococcal activity of the azo-dye, *protonsil rubrum*. In the body, protonsil is reduced to sulphanilamide which is widely used to combat pneumonia, gonorrhoea, etc. Derivatives of sulphanilamide (commonly called *sulpha drugs*) are more effective or specific.

(10) The amino H atoms of aniline are replaced by potassium (or sodium) when it is heated with the metal— C_6H_5NHK and $C_6H_5NK_2$ are thus obtained.

Salvarsan, 606 or *p*-dihydroxy-*m*-diamino-arsenobenzene dihydrochloride: Phenol is arsenated by heating with arsenic acid, the product formed is nitrated. With sodium hyposulphite, $Na_2S_2O_4$, the nitro group is reduced to amino group and the arsenic acid group to $-As=As-$; two such reduced mols. then combine to give salvarsan base. The dihydrochloride is used in medicine to combat syphilis and malaria tertiana. It readily decomposes in air and so is kept in evacuated tubes or in an inert gas. Paul Ehrlich, the father of chemotherapy, discovered salvarsan in 1910; it was the 606th atoxyl (p. 357) derivative synthesised in his laboratory.



Tests.—(i) On warming aniline with chloroform and alcoholic caustic potash, phenyl isocyanide with a repulsive odour is formed (p. 79). But any primary amine, aliphatic or aromatic, gives this test.

(ii) On shaking 1-2 drops of aniline with 10 c.c. of water and adding to it a little bleaching powder solution, a transient violet colour is produced, which soon turns brown and fades away. Only *free* aniline, in aqueous solution, gives this characteristic test.

(iii) On adding a drop of a dilute potassium dichromate solution to a solution of aniline in H_2SO_4 , a red colour is produced, which slowly turns deep blue.

(iv) Ligno-celluloses (e.g., jute, wood, etc.) give a yellow coloration with aniline salts.

(v) **Diazo-reaction**: To a well-cooled solution of aniline hydrochloride containing an excess of hydrochloric acid, a few drops of sodium nitrite solution are added. With β -naphthol (in excess of caustic soda), a brilliant red dye is produced. All primary aromatic amines give this test.

Uses.—Aniline is employed in making *aniline dyes*, synthetic indigo, stains such as safranine, rosaniline blue, etc., drugs like *atoxyl* (a remedy for sleeping sickness; it is the sodium salt of arsanilic acid, $\text{H}_2\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}_3\text{H}_2$), *antifebrin*, sulpha drugs, etc. It is an important accelerator for vulcanisation of rubber.

General properties.—Primary aromatic amines are colourless liquids or solids with a faint smell which is not ammoniacal. They are practically insoluble in water but dissolve in many organic solvents. The amines gradually turn brown or black on exposure to air and light. They are volatile in steam and distil without decomposition. They are very weak bases—neutral to litmus—but form crystalline salts with acids and crystalline double-salts with platinic chloride. Chemically, all of them behave like aniline. They give diazo-salts with nitrous acid in the cold, respond to the carbylamine reaction, form condensation products with carbon disulphide, aldehydes, etc., produce anilides with acid chlorides, and so on.

Acetanilide, phenylacetamide or antifebrin, $\text{C}_6\text{H}_5\text{NHOCCH}_3$, is made by acetylating aniline with glacial acetic acid, acetyl chloride or acetic anhydride.



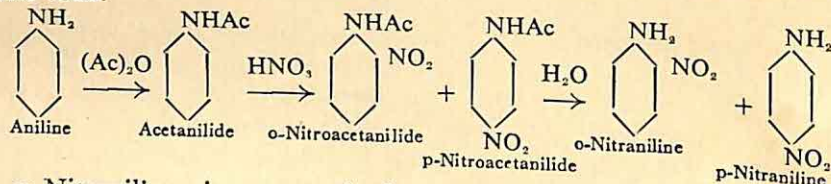
Freshly distilled aniline (10 c.c.) and glacial acetic acid (20 c.c.) are gently boiled for about an hour in a conical flask (150 c.c.) provided with a reflux condenser. The hot liquid is poured into cold water (200 c.c.) with stirring during addition. Acetanilide crystals separate. These are recrystallised from boiling water or dilute alcohol. The yield is quite high.

Acetanilide forms white, rhombic plates (m.p. 114°), sparingly soluble in cold, but readily soluble in hot, water. It was formerly used for lowering the body temperature and so called *antifebrin*. It also relieves headache and neuralgic pain but affects the heart. It has been largely replaced by better drugs. On hydrolysis with alkalis or, better with acids, it gives back aniline and acetic acid (cf., hydrolysis of acetamide, p. 166).

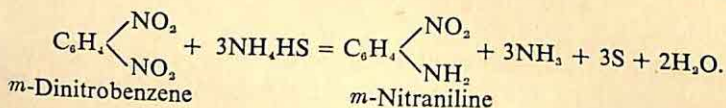
Sulphanilic acid, *p*-aminobenzenesulphonic acid, $\text{C}_6\text{H}_4(\text{NH}_2)\text{SO}_3\text{H}$, is prepared, as already mentioned, by heating aniline sulphate with

fuming H_2SO_4 to about 200° for nearly five hours. It forms colourless crystals (with 2 mols. of water), sparingly soluble in cold, but readily soluble in boiling water. It decomposes on heating before melting. It forms salts with alkalis but not with acids. The free acid (though not its dry sodium salt) is difficult to acetylate. This is because sulphanilic acid exists as an internal salt, $\text{H}_3\text{N}^+\text{-C}_6\text{H}_4\text{-SO}_3^-$, (zwitter-ion) like amino-acids (p. 185). On heating with soda-lime, it gives aniline. Certain azo-dyes, e.g., methyl orange (q.v.) are made from it. *p*-Aminobenzene-sulphonyl derivative of *n*-butylurea, taken orally, lowers the blood sugar of diabetics, like insulin which has to be injected.

Nitranilines, $\text{NH}_2\text{C}_6\text{H}_4\text{NO}_2$, (*o*-, *m*- and *p*-) cannot be obtained by the direct nitration of aniline as nitric acid oxidises the amino group. If, however, the amino group is 'protected' by acetylation, fuming HNO_3 at low temperature gives *o*- and *p*-nitro-derivatives, the latter predominating (90%). These are easily separated as the *o*-compound is soluble in ice-cold water but not the *p*-. Free nitranilines are obtained therefrom by hydrolysis with conc. HCl and subsequent treatment with caustic soda.

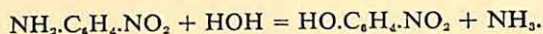


m-Nitraniline is prepared from *m*-dinitrobenzene by partial reduction with alcoholic ammonium hydrosulphide. Sulphuretted hydrogen is passed into an alcoholic solution of *m*-nitraniline and ammonia; the mixture is warmed on water-bath. The yield is about 80%.



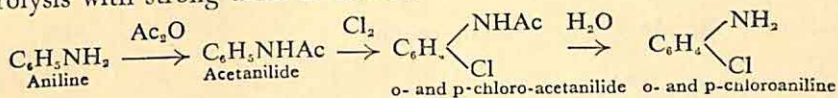
This is, however, more readily effected by boiling *m*-dinitrobenzene in aqueous suspension with sodium disulphide, Na_2S_2 , solution (made by adding S to Na_2S). Peculiarly, however, if aniline is nitrated in strong H_2SO_4 , mainly *m*- and only a little *p*- and *o*-nitraniline are formed. *p*-Nitraniline is made by the action of aqueous ammonia on *p*-nitrochlorobenzene (made by nitrating chlorobenzene) at 170° in an autoclave with stirring (cf., formation of aniline from chlorobenzene, p. 353).

Nitranilines are orange-yellow, crystalline solids; the ortho-compound melts at 71° while the meta- and para- at 114° and 147° respectively. Their basic character has been weakened by the electron-attracting $-\text{NO}_2$ group (p. 352); they dissolve only in excess of acid to form salts which, when pure, are colourless. They are not, however, equally basic—the *o*-compound is the weakest, and the *m*- the strongest. They are sparingly soluble in water but dissolve readily in alcohol. On reduction, they yield the corresponding diamino-compounds called phenylenediamines. Boiling aqueous caustic alkalis convert *o*- and *p*-nitranilines to *o*- and *p*-nitrophenols—a remarkable change.



p-Nitraniline is commercially important for making *para-red*; *p*-phenylenediamine is the parent compound of many dyes. Some azo-dyes are derived from *m*-nitraniline.

Chloro- and bromo-anilines.—Trichloro- and tribromo-anilines are formed by the direct action of the halogens on aniline (p. 355). So the monohalogen-derivatives cannot be obtained thus. The amino group in aniline is first 'protected' by acetylation, chlorine (or bromine) then yields the *o*- and *p*-derivatives. The *p*-compound is the main product. These are separated by fractional crystallisation, followed by hydrolysis with strong acids or alkalis.

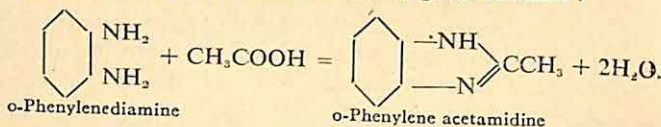


m-Chloro-aniline is conveniently obtained by reduction in acid solution of *m*-chloronitrobenzene, $\text{Cl}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$. By chlorinating (or brominating) aniline in presence of a large excess of conc. H_2SO_4 , *m*-chloro- (or bromo-) aniline is also obtained (cf., formation of *m*-nitraniline, p. 358). *p*-Chloroaniline is a solid (m.p. 71°) and *o*- and *m*-isomers are liquids boiling at 207° and 236° respectively. They have little technical importance.

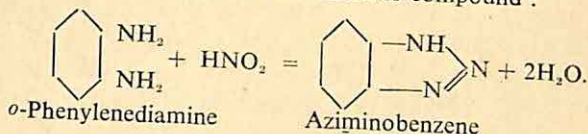
Toluidines, aminotoluenes, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3$, are homologues rather than derivatives, of aniline. They are prepared like aniline. Nitro-toluenes (*o*-, *m*- and *p*-), on reduction with tin (or iron) and hydrochloric acid, yield the corresponding aminotoluenes. *p*-Toluidine is a white, crystalline solid (m.p. 43° , b.p. 200°) while *o*- and *m*-compounds are liquids, both boiling at 199° . They closely resemble aniline—give diazo-salts, form acetyl derivatives, yield salts with acids, produce thiocarbamilides, etc., and also respond to the isocyanide test. Triphenylmethane dyes are made from *o*- and *p*-toluidines. Toluidines are identified by their acetyl derivatives; *o*-, *m*- and *p*-acetotoluidines melt at 110° , 65° and 153° respectively. They may be separated by fractional crystallisation of their acetyl derivatives.

Phenylenediamines, diaminobenzenes, $\text{C}_6\text{H}_4(\text{NH}_2)_2$, are primary amines ($-\text{C}_6\text{H}_4-$ is called *phenylene* group). The ortho- and para-isomers are prepared by the reduction of corresponding nitranilines but the meta-derivative is usually made by reducing *m*-dinitrobenzene. They are all white, crystalline solids which darken on exposure to light and air due to oxidation but their salts are more stable. They are soluble in hot water. The *o*-, *m*- and *p*-compounds melt respectively at 102° , 63° and 140° ; they are weak bases like aniline. *m*-Diamine is used for making azo-dyes and the para- for safranine and indamine dyes. *m*-Phenylenediamine gives with a trace of nitrous acid a yellow-brown coloration (*Bismarck brown*), and is employed in water-analysis for the detection and colorimetric estimation of nitrites. The *p*-diamine readily forms benzoquinone, $\text{C}_6\text{H}_4\text{O}_2$, on oxidation. The diamines give the common reactions of primary aromatic amines. *o*-Diamine, however, forms rings due to the proximity of the amino groups, e.g.,

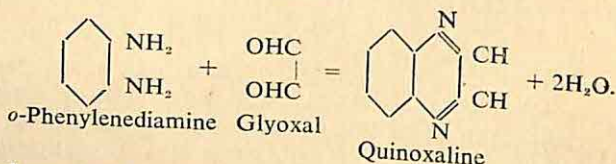
(i) On heating with acetic acid, *o*-diamine gives amidine :



(ii) With nitrous acid, it forms an azimino-compound :

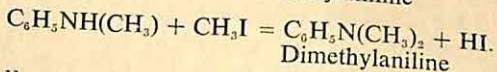
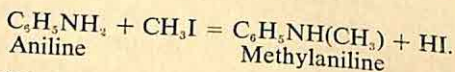


(iii) With glyoxal, quinoxaline results :



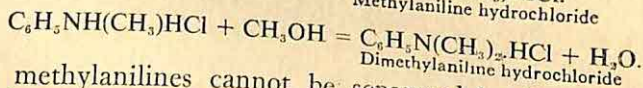
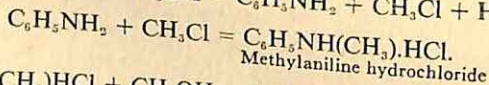
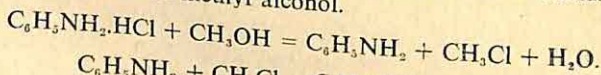
Secondary and tertiary aromatic amines.—The secondary aromatic amines contain the imino group, —NH— , which may be linked to two aryl groups as in diphenylamine, $(\text{C}_6\text{H}_5)_2\text{NH}$, or to one aryl and one alkyl group as in methylaniline, $\text{C}_6\text{H}_5\text{NH}(\text{CH}_3)$.

Methylaniline, $\text{C}_6\text{H}_5\text{NH}(\text{CH}_3)$, is formed together with dimethylaniline, $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$, on heating aniline under pressure with methyl iodide (*cf.*, preparation of aliphatic amines from NH_3 and alkyl halides, p. 206).



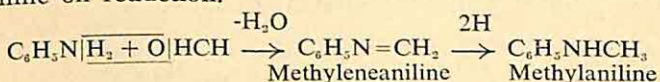
Commercially, it is made by heating under pressure the requisite quantities of aniline, methyl alcohol and a little H_2SO_4 or HCl to about 230° . Some dimethylaniline is also produced.

Aniline forms a salt with the acid, which reacts with methanol to give methyl chloride (say). The latter methylates aniline. At high temperature, the methyl group migrates from the nitrogen to the para-position (p. 362). Dimethylaniline, which is technically important, is almost exclusively formed if there is a large excess of methyl alcohol.



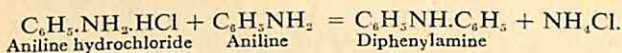
The methylanilines cannot be separated by fractional distillation as both boil at 192° . The mixture is acetylated, monomethylaniline forms an acetyl derivative but not the other. On distillation, dimethylaniline passes over leaving behind the acetyl derivative which, on

alkaline hydrolysis, yields monomethylaniline. Pure monomethylaniline is obtained by reacting aniline and formaldehyde in presence of warm caustic soda and zinc dust. Methylenedianiline, first formed, gives methylaniline on reduction.

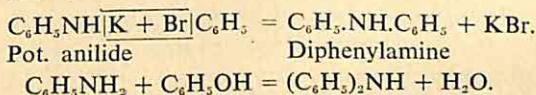


Monomethylaniline, largely used in making dyestuffs, is a colourless oil (b.p. 192°) lighter than water. The $-\text{CH}_3$ group makes it a slightly stronger base ($k_b = 7.1 \times 10^{-10}$) than aniline (p. 351). With nitrous acid, it gives methylphenylnitrosoamine, $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)\text{NO}$, a light yellow oil (cf., alkyl nitrosoamine, p. 207).

Diphenylamine, $(\text{C}_6\text{H}_5)_2\text{NH}$, is commercially obtained by heating aniline hydrochloride with aniline in a closed vessel to about 240° .

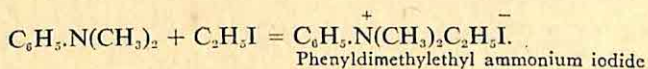


It is also formed when bromobenzene is heated with aniline and copper powder (p. 362), or potassium anilide (p. 356) is treated with bromobenzene. Heated with phenol and zinc chloride to 260° , aniline yields diphenylamine.

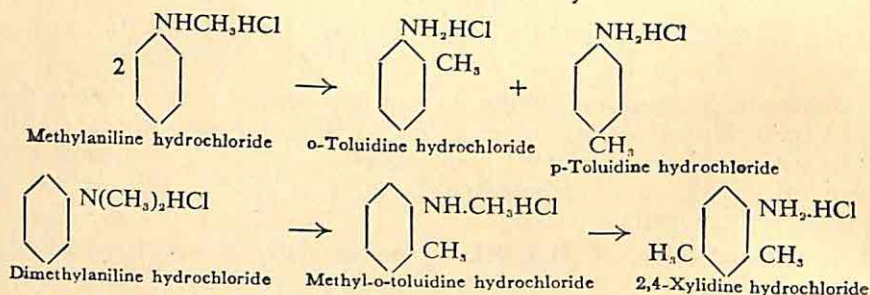


Diphenylamine forms colourless crystals (m.p. 54°), insoluble in water but soluble in alcohol and ether. A second C_6H_5 - group makes it a much weaker base than aniline (p. 351), its salts are decomposed by water. The H of the imino group can be replaced by metallic potassium (or sodium)—pot. diphenylamine, $(\text{C}_6\text{H}_5)_2\text{NK}$, is thus obtained. Diphenylamine in conc. H_2SO_4 produces a deep blue coloration with traces of nitric acid and is occasionally used for its detection. It is an internal indicator in some oxidation-reduction methods (e.g., the volumetric estimation of iron with dichromate), and the principal stabiliser for smokeless powder (p. 292). It gives an acetyl derivative and also forms a nitrosoamine with nitrous acid. Diphenylamine is insoluble in dilute acid. For its very high b.p. (302°), it is sometimes used in Victor Meyer's apparatus for determining mol. wts. Some dyes are made from it.

Dimethylaniline, $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$, the simplest mixed tertiary amine (p. 360), is a colourless, oily liquid (b.p. 192°). It is a strong base ($k_b = 1.1 \times 10^{-9}$) due to the presence of two methyl groups (p. 351), forming salts with acids. Having no hydrogen in the amino group, it cannot form an acetyl derivative. It, however, gives a green nitroso-derivative (p. 363) with HNO_2 , and so, differs from aliphatic tertiary amines. With alkyl iodides, it yields quaternary ammonium compounds:

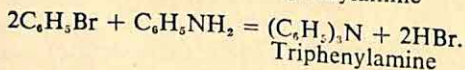
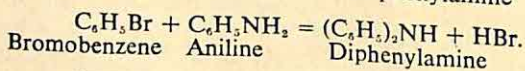
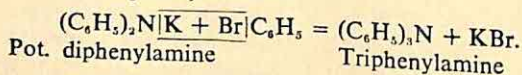


Alkyl groups attached to the nitrogen in aromatic amines sometimes migrate to the nucleus. For example, methylaniline hydrochloride, heated in a closed vessel above 300° , gives a mixture of *p*- and *o*-toluidines. Dimethylaniline behaves similarly.

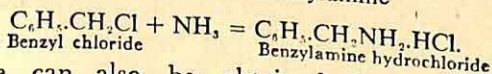
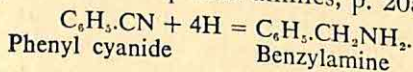


Xylidine (b.p. 212°) is thus commercially made for dye manufacture. Dimethylaniline also makes some valuable dyes. It forms with aqueous hydrogen peroxide dimethylaniline oxide, $(\text{C}_6\text{H}_5)_2\text{N} \rightarrow \text{O}$, (*cf.*, amine oxide, p. 208).

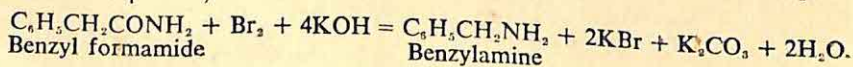
Triphenylamine, $(\text{C}_6\text{H}_5)_3\text{N}$, a purely aromatic tertiary amine, is a colourless, crystalline solid (m.p. 127°). It dissolves in conc. H_2SO_4 with a blue colour. It forms neither quaternary compounds with alkyl iodides nor salts with acids. Triphenylamine may be prepared by heating potassium diphenylamine (or dipotassium anilide, $\text{C}_6\text{H}_5\text{NK}_2$), with bromobenzene, or diphenylamine with iodobenzene and copper powder. Aniline, heated with bromobenzene in presence of copper powder, forms both di- and triphenylamine.



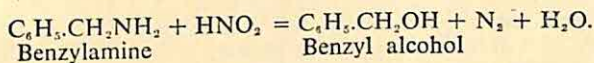
Benzylamine, aminotoluene, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$, which is isomeric with the toluidines, has the amino group in the side-chain. It behaves like an aliphatic amine and is similarly prepared. Benzylamine together with di- and tri-benzylamine results on reducing phenyl cyanide with sodium and alcohol, or heating benzyl chloride with ammonia under pressure (*cf.*, preparation of aliphatic amines, p. 205).



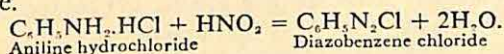
Benzylamine can also be obtained from benzyl formamide, $\text{C}_6\text{H}_5\text{CH}_2\text{CONH}_2$, by reacting with bromine and caustic potash (Hofmann, p. 203).



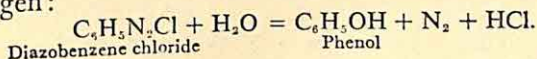
It is a colourless liquid (b.p. 185° , sp. gr. 0.981) with a pungent, ammoniacal smell, soluble in water. It is quite a strong base ($k = 2.3 \times 10^{-5}$), alkaline to litmus (contrast to aniline) and forms stable salts with acids. Benzylamine gives the isocyanide test. With nitrous acid, it forms no diazo-salt (distinction from isomeric toluidines) but yields benzyl alcohol and nitrogen (*cf.*, action of HNO_2 on methylamine, p. 204). It is a dye intermediate.



Distinction between primary, secondary and tertiary amines.—This is done with nitrous acid (*cf.*, aliphatic amines, p. 209). (1) Primary aromatic amines (as salts) form diazo-compounds with nitrous acid at low temperature.

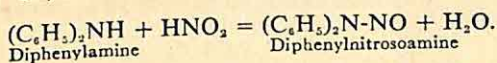


This, on coupling with β -naphthol in caustic soda, gives a brilliant red dye. On warming, the diazo-salt decomposes to a hydroxy-derivative and nitrogen:



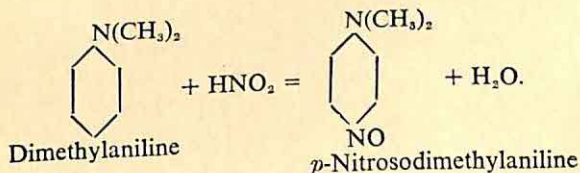
Primary amines alone give the carbylamine test with chloroform and alcoholic potash (p. 355); they also yield condensation products with carbon disulphide (p. 355).

(2) Secondary amines react with nitrous acid to produce a nitrosoamine, a yellow oil, insoluble in ether.



Liebermann's reaction.—On warming a drop of the nitroso-compound with phenol in conc. H_2SO_4 , a blue colour is developed. With water, it turns red which changes to blue again on adding caustic soda solution.

(3) Tertiary amines such as dimethylaniline, react with nitrous acid to form *p*-nitroso-derivatives. But aliphatic tertiary amines do not react with nitrous acid (p. 208). A purely aromatic tertiary amine such as triphenylamine, $(\text{C}_6\text{H}_5)_3\text{N}$, does not, however, react with nitrous acid.



Amines can also be identified by other reactions. For example, only primary amines give the isocyanide test. Primary and secondary amines yield acetyl derivatives but not the tertiary. Tertiary aromatic amines, having an alkyl group linked to nitrogen, form quaternary ammonium compounds with alkyl iodides. Hinsberg's test for distinguishing between primary, secondary and tertiary amines (p. 211) is also applicable to aromatic amines.

QUESTIONS

1. How is aniline obtained? Describe the action of bromine, nitric acid, sulphuric acid and nitrous acid on aniline. Compare and contrast the properties and reactions of aniline and methylamine. (B.Sc. Pass, 1936, Allahabad Uni., B.Sc. 1952, Gauhati Uni.).

2. Describe the reactions of nitrous acid with hydrochloric acid solutions of primary, secondary and tertiary amines of both aliphatic and aromatic series. (B.Sc., London, 1931).

3. Compare the properties of the following: (a) ethylamine and *p*-toluidine, and (b) *o*-toluidine and benzylamine.

4. Starting from aniline, how would you prepare (a) *o*-toluidine, (b) diphenylamine, (c) *p*-nitraniline, and (d) sulphanilic acid?

5. Describe the properties of arylamines and show clearly the points of difference between these and the properties of alkylamines. Give an outline of the uses of arylamines. (B.A. Degree Exam., 1942, Madras Uni.).

6. By what reactions could you distinguish between primary, secondary and tertiary amines? In what respects do the aliphatic amines differ from the aromatic amines? (B.Sc. Pass, 1932, Dacca Uni.).

7. How will you prepare from benzene: (a) benzoic acid, (b) benzyl chloride, (c) aniline, and (d) chlorobenzene? (B.A. Pass, 1938, Bombay University).

8. How is aniline prepared on a large scale? State its uses. Starting from aniline, how would you obtain (a) benzene, (b) phenol, and (c) monobromo-benzene? (B.Sc. Pass, Calcutta Uni.).

9. How would you prepare a specimen of acetanilide in the laboratory? (B.Sc., 1922, Punjab Uni.).

10. Give an outline of the process of manufacture of aniline. (B.Sc., 1936, Punjab Uni.).

11. You are given a mixture of chlorobenzene, phenol and aniline in ether. Describe carefully how you would proceed in order to separate the constituents of the mixture and obtain each in pure condition. (B.Sc. Degree Exam., 1941, Travancore Uni.).

12. A neutral compound containing 71.1% C, 6.7% H and 10.4% N, gave, on hydrolysis with conc. HCl, a monoacidic amine, the platinichloride of which had 32.7% Pt. What is its probable structure? Ans. $C_6H_5NH.CO.CH_3$.

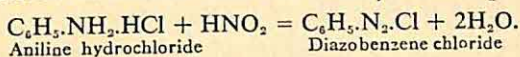
13. Two compounds *A* and *B*, each having 63.58% C, 5.96% H and 9.27% N, give benzoic acid on oxidation. Both dissolve in NaOH solution with a red colour. On reduction, *A* & *B* yield two amines *X* and *Y*, respectively. *X* but not *Y* can be resolved into optical isomers. What are *A* & *B*?

Ans. $C_6H_5.CH(NO_2).CH_3$; $C_6H_5.CH_2.CH_2.NO_2$.

CHAPTER XXXVI

THE DIAZO-COMPOUNDS

A salt of aniline or any other aromatic primary amine with the $-NH_2$ group attached to the nucleus, reacts with nitrous acid at *low* temperature and forms a diazo-salt. Aliphatic primary amines give no diazo-salt under these conditions but split up into an alcohol and nitrogen (*cf.*, action of nitrous acid on methylamine, p. 204).

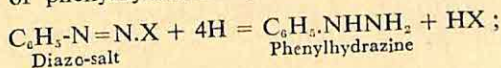


This is *diazo-reaction*, discovered in 1858 by the German chemist, Peter Griess (1829-88), while working in Hofmann's laboratory in London. The product is called *diazo-compound*, for it has the di-azo group, $-N_2-$ (French *azote*, nitrogen). It is one of the most important organic reactions, technically and in the laboratory—many benzene derivatives and azo-dyes are made from diazo-salts. The diazo-compound is prepared by dissolving the amine (1 molecular equivalent) in excess of H_2SO_4 or HCl ($2\frac{1}{2}$ equivalents) and adding an aqueous solution of sodium nitrite (1 equivalent) in the cold.

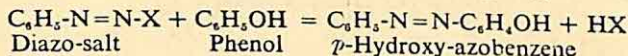
Preparation.—Nitrous acid is made *in situ* from sodium nitrite and dilute HCl . Aniline (15 c.c.), dissolved in hydrochloric acid (40 c.c. conc. HCl in 40 c.c. of water), is cooled to about 5° and an aqueous solution of sodium nitrite (12.5 g. in 30 c.c. of water) is slowly added to it with frequent stirring. If the temperature rises above 10° , the diazo-salt decomposes to phenol. The addition of nitrite is stopped when starch-iodide paper *immediately* turns blue with the reaction mixture, showing the presence of free nitrous acid. The liquid turns pale yellow, diazobenzene chloride formed remains in solution. The process is called *diazotisation*. The aqueous solution is generally employed for preparing various benzene derivatives.

Solid diazobenzene hydrogen sulphate.—Aniline (15 g.) is dissolved in absolute alcohol (150 c.c.) and conc. H_2SO_4 (16 c.c.) is slowly added with stirring. The solution of aniline sulphate is cooled to about 30° and amyl nitrite, $C_5H_{11}ONO$, (20 g.) is added *drop by drop* with stirring. The temperature is maintained between 25° - 35° ; when all the amyl nitrite has been added, the liquid is allowed to stand for about 15 minutes. It is cooled in crushed ice, when diazobenzene hydrogen sulphate, $C_6H_5N_2HSO_4$, separates in greenish white crystals. It is filtered at the pump, washed with absolute alcohol, and dried by pressing on filter paper, but *not* in a drying oven. Though quite harmless in aqueous solution, dry diazo-salts may explode. Nitrous acid comes from sulphuric acid and amyl nitrite.

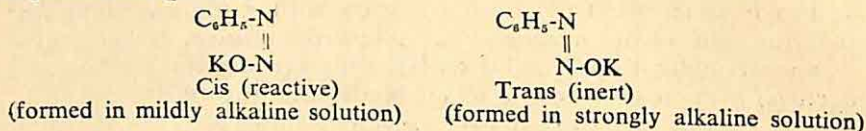
Constitution of diazo-compounds.—From analysis, a diazobenzene salt is $C_6H_5N_2X$, X being an acid radical e.g., Cl^- , NO_3^- , HSO_4^- , etc. The nitrogen atoms and X form a monovalent group, because (i) a penta-substituted aniline forms a diazo-salt, and (ii) on decomposition, diazo-salts from aniline *always* yield mono-substituted benzene derivatives such as C_6H_5Cl , etc. On reduction, diazobenzene chloride forms phenylhydrazine, $C_6H_5.NH.NH_2$. Two structures are important, viz. $C_6H_5-N=N-X$, due to Kekulé (1866), which readily explains (i) the formation of phenylhydrazine by the reduction of a diazobenzene salt:



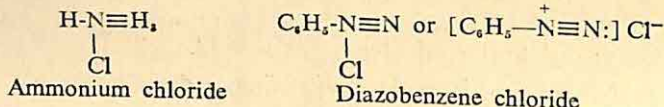
(ii) the formation of azo-dyes which contain the group, $-N=N-$



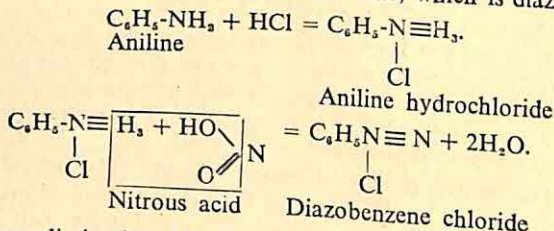
(iii) the existence of two isomeric diazotates formed on adding excess of caustic alkali to a diazo-salt. According to Hantzsch (1895), their isomerism is geometrical (p. 337).



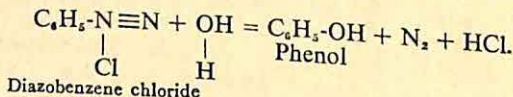
The second structure is due to Blomstrand (1869) who showed close analogy between diazo-salts and ammonium salts, and suggested that there must be at least one salt-forming or 'pentavalent' nitrogen in the molecule. Thus (i) Both ammonium salts and diazo-salts are colourless, crystalline, soluble in water and insoluble in organic solvents generally. They form similar platinum and gold double salts. (ii) The salts, obtained from strong acids, e.g., NH_4Cl and $\text{C}_6\text{H}_5\text{N}_2\text{Cl}$, are neutral; but those from weak acids are alkaline, e.g., carbonates, acetates, etc. (iii) Their ionisation constants are practically the same, they dissociate into two ions. They are, therefore, represented as



That is why diazobenzene salts are called diazonium salts. It also explains (†) that it is the salt of aniline, but not free aniline, which is diazotised:

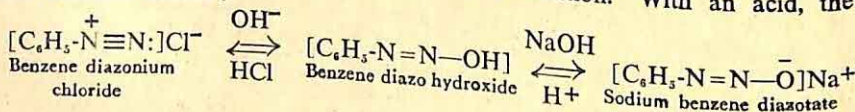


(ii) the easy elimination of nitrogen, and formation of mono-derivatives of benzene from diazo-salts:



Infra-red absorption spectra of diazonium salts indicate the presence of a triple bond in them. But the formation of azo-compounds, diazotates, and phenylhydrazine is better accounted for by Kekulé's constitution.

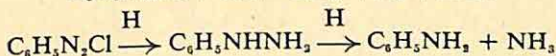
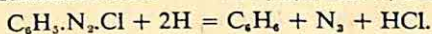
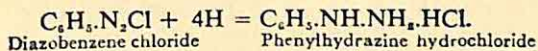
With caustic soda, a diazonium salt gives the hydroxide which exists in very dilute solution only; it stabilises itself by salt formation. With an acid, the reverse reaction occurs:



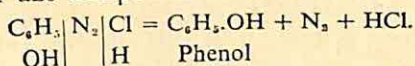
Properties.—Diazonium salts are generally colourless and crystalline, readily soluble in water but less so in alcohol. They are unstable

and readily yield a variety of products with different reagents. The dry salts explode violently on heating.

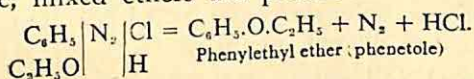
Reactions.—(i) On reduction at low temperature with stannous chloride in hydrochloric acid, or sodium sulphite, diazobenzene chloride yields phenylhydrazine. Alkaline stannous chloride, however, reduces it to benzene. With zinc and hydrochloric acid, we get aniline.



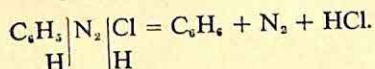
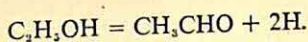
(ii) Warmed in aqueous solution to 40°-50°, diazo-salts give phenol; the yield is better from the sulphate. If the solution is not strongly acid, the phenol formed couples with the undecomposed diazo-salt, and an azo-compound results.



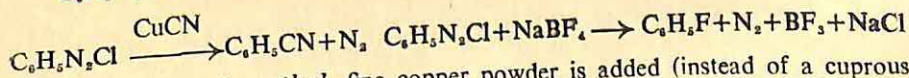
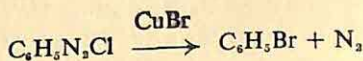
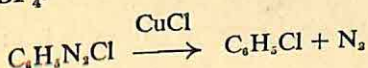
(iii) On heating an *absolute* alcoholic solution of *anhydrous* diazobenzene chloride, mixed ethers are produced.



By a side-reaction, some of the alcohol is oxidised to aldehyde and the diazo-salt reduced to benzene. With methanol, however, no benzene results; the only product is phenylmethyl ether. This reduction is better effected by hypophosphorous acid or alkaline sodium stannite. An amino group in benzene ring can thus be replaced by hydrogen.

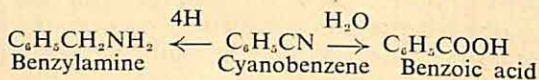


(iv) Phenyl halides are easily obtained by warming diazobenzene chloride with (a) cuprous chloride in HCl, and (b) cuprous bromide in HBr. Similarly, cyanobenzene is formed when the diazo-salt is warmed with cuprous cyanide in aqueous pot. cyanide. The halogen of copper halide goes to the nucleus. These are known as *Sandmeyer's reaction*, the mechanism of which is not quite clear. The cuprous salt probably first forms an unstable additive compound with the diazo-salt, which then decomposes to yield various products. Fluorobenzene is obtained by warming diazobenzene chloride with sodium fluoroborate, NaBF₄.

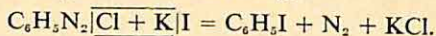


In *Gattermann's method*, fine copper powder is added (instead of a cuprous salt) to the acid solution of the diazo-salt—the above reactions then take place

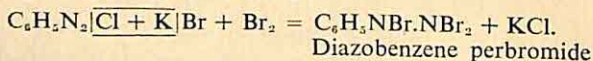
at room temperature and sometimes give better yield. The last reaction is important for the preparation of aryl cyanides which cannot be obtained by the interaction of aryl halides and potassium cyanide. Cyanobenzene thus obtained, may be hydrolysed to benzoic acid, or reduced to benzylamine.



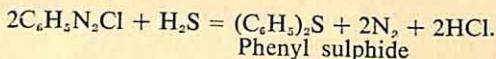
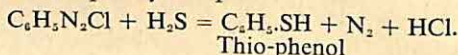
(v) Iodobenzene is, however, best obtained by adding warm aqueous potassium iodide or hydriodic acid to the diazo-salt, no copper salt is necessary. The yield is about 80%.



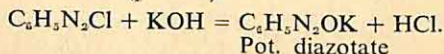
(vi) On mixing in the cold a solution of bromine in potassium bromide to the solution of diazobenzene chloride, diazobenzene perbromide crystals separate, which, on boiling in alcoholic solution, decompose to bromobenzene. With aqueous ammonia, the perbromide yields phenyl azide, $\text{C}_6\text{H}_5\text{N}_3$.



(vii) Diazobenzene chloride combines with sulphuretted hydrogen to give thiophenol and phenyl sulphide.



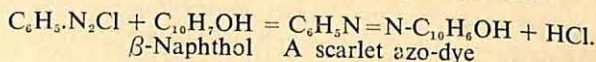
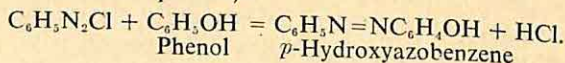
(viii) It reacts with potassium hydroxide solution in excess and yields potassium diazotate (p. 366).



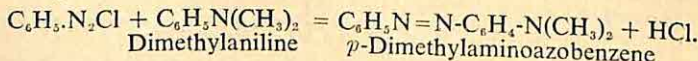
(ix) With copper powder and ethanol, diphenyl is formed:



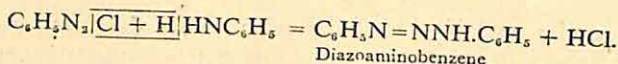
(x) Diazo-salts react (or 'couple') with phenols and other aromatic hydroxy-derivatives, in alkaline medium, to yield brilliant azo-dyes. These reactions are valuable for detecting aromatic primary amines (cf., detection of aniline, p. 357).



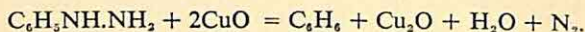
(xi) Aromatic amines form different types of products with diazobenzene chloride: (a) dimethylaniline, in presence of dilute acid, gives dimethylaminoazobenzene:



(b) aniline and diazobenzene chloride yield diazoaminobenzene (p. 370).

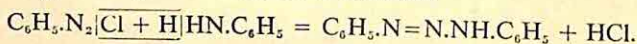


to air. It melts at 23° and boils with slight decomposition at 241° . It is almost insoluble in water, but soluble in common organic solvents. It is strongly basic and forms white, crystalline salts with acids. Phenylhydrazine is a poison, it causes eczema on frequent contact with the skin. It is a strong reducing agent, it reduces Fehling's solution *in the cold*:



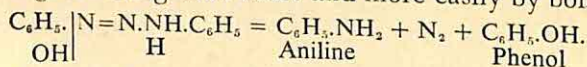
The same change is brought about by heating phenylhydrazine with copper sulphate or ferric chloride solution. Benzene may thus be obtained from aniline or nitrobenzene. The reactions of phenylhydrazine with carbonyl compounds such as aldehydes (p. 129), ketones (p. 138) and simple sugars (p. 275) are important. *p*-Bromo- and *p*-nitro-phenylhydrazine give hydrazones which are more easy to crystallise and also less soluble. Powerful reducing agents such as zinc dust and HCl, convert phenylhydrazine into aniline and ammonia. The constitution of phenylhydrazine follows from this and its formation from a diazo-salt. *Antipyrine* and some dyes are made from phenylhydrazine.

Diazoaminobenzene, $\text{C}_6\text{H}_5\text{.N=N.NHC}_6\text{H}_5$.—As already mentioned, diazonium salts react with primary or secondary aromatic amines to form diazoamino-compounds. When aniline is added to diazobenzene chloride in equimolecular proportion, diazoaminobenzene separates in fine, golden yellow needles. These are filtered, washed with water, dried and re-crystallised from benzene. Sodium acetate accelerates the reaction by neutralising the hydrochloric acid formed.

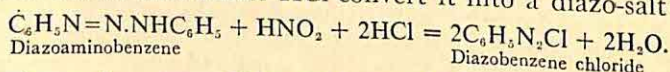


Diazoaminobenzene

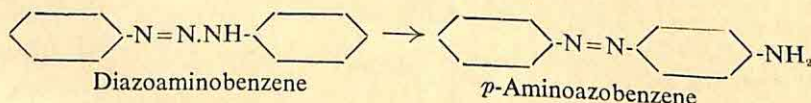
With excess of diazo-salt, a di-substituted compound, $(\text{C}_6\text{H}_5\text{.N}_2)_2\text{N.C}_6\text{H}_5$, is formed. When sodium nitrite acts on *excess* of aniline hydrochloride in aqueous solution, diazobenzene chloride formed reacts with the unchanged aniline to give diazoaminobenzene. It has two forms, melting at 80° and 98° . It explodes on heating rapidly. It is slightly soluble in water but readily soluble in alcohol, ether and benzene. It is a feeble base, and is hydrolysed to phenol and aniline on prolonged boiling with water and more easily by boiling dilute H_2SO_4 .



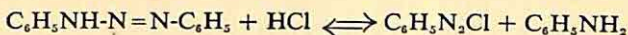
Sodium nitrite and excess HCl convert it into a diazo-salt:



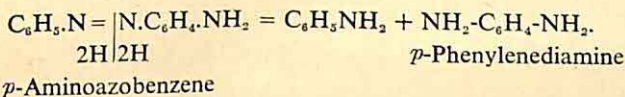
***p*-Aminoazobenzene**, $\text{C}_6\text{H}_5\text{N=NC}_6\text{H}_4\text{NH}_2$.—When diazoaminobenzene in aniline solution is warmed to about 40° for a short while with a little aniline hydrochloride, *p*-aminoazobenzene is formed (cf. formation of *p*-toluidine from methylaniline, p. 362).



The mechanism of the change is obscure; it is believed to be intermolecular and proceed as



Aniline hydrochloride, the catalyst, supplies the proton; the diazonium ion, in acid solution, reacts at the *p*-position of aniline or the *o*-position (but more slowly) if the para is occupied. On adding HCl, *p*-aminoazobenzene hydrochloride separates in steel-blue needles. The free base is liberated with dilute ammonia. From alcohol, *p*-aminoazobenzene crystallises in orange-red plates (m.p. 127°). It is also obtained by nitrating azo-benzene, $\text{C}_6\text{H}_5\cdot\text{N}=\text{N}\cdot\text{C}_6\text{H}_5$, and reducing the *p*-nitroazobenzene, $\text{C}_6\text{H}_5\text{N}=\text{N}\cdot\text{C}_6\text{H}_4\text{NO}_2$, formed with alcoholic ammonium sulphide. It is thus an amino-derivative of azobenzene. *p*-Aminoazobenzene is the parent substance of *chrysoidine* dyes. Manganese dioxide and sulphuric acid oxidise it to *p*-benzoquinone, $\text{O}:\text{C}_6\text{H}_4:\text{O}$. On reduction with tin and HCl, it decomposes into aniline and *p*-phenylenediamine, which supports its constitution.



QUESTIONS

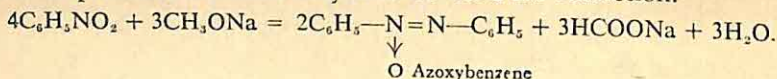
- How can you obtain (i) benzene from nitrobenzene, (ii) benzylamine from aniline, (iii) thio-phenol from aniline, (iv) aniline from phenylhydrazine, (v) phenylhydrazine from benzene and (vi) benzoic acid from benzene?
- Describe how you would prepare a diazo-solution starting with 10 g. of aniline. How would you use such a solution to prepare (a) benzo-nitrile, (b) phenylhydrazine, (c) benzene-azo-dimethyl aniline? B.Sc. London.
- Indicate by an equation or equations, the process which is thought to occur when an aromatic base, $\text{R}\cdot\text{NH}_2$, is diazotised. Classify the uses to which diazo-compounds may be put, give examples of each reaction. B.Sc., London.
- What do you understand by diazotisation? Show how with the help of this reaction various substituents can be introduced into the benzene nucleus. B.A. & B.Sc., 1938, Bombay Uni.
- Discuss the constitution of aromatic diazo-compounds. B.Sc., Hons., 1934, Dacca Uni.
- Describe briefly the reactions which go after the names of (a) Fittig, (b) Friedel-Crafts, (c) Sandmeyer, and (d) Liebermann. B.Sc., Pass, 1931, Allahabad Uni.
- Give the essential practical details for the diazotisation of aniline. Indicate by equations, the main reactions of diazonium compounds. B.A. Pass, 1937, Bombay Uni.
- What are the conditions necessary for the preparation of diazonium salts? Starting with an aqueous solution of diazobenzene chloride, how may the following be prepared: (a) benzene, (b) phenol, (c) benzoic acid, (d) phenylhydrazine, and *p*-amino-azobenzene? B.Sc. Degree Exam., 1942, Annamalai Uni.
- How is benzene diazonium sulphate prepared? Give its properties and reactions. Discuss its constitution and give its uses. B.Sc., 1941, Agra Uni.; B.Sc. Exam. 1945, Benares Hindu Uni.
- What are diazo-compounds? Indicate their importance in industry and in synthetic chemistry. B.Sc. Exam. (Principal paper) Bombay Uni. 1947.

THE AZO-COMPOUNDS

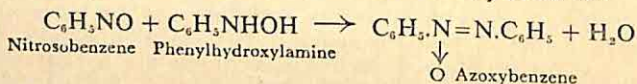
In azo-compounds, a $-N=N-$ group links up two aromatic nuclei. The simplest is azobenzene, $C_6H_5-N=N-C_6H_5$; aminoazobenzene, $C_6H_5-N=N-C_6H_4NH_2$, is another (p. 370). These are much more stable than diazo-compounds due to the linking of the nitrogen atoms to different benzene rings. They include the well-known azo-dyes and are commercially important. Prontosil, once a valuable drug, is an azo-dye obtained from *p*-aminobenzenesulphonamide.

Azoxybenzene, $\text{C}_6\text{H}_5\text{-}\overset{\text{O}}{\underset{\text{O}}{\text{N}}}\text{-N-C}_6\text{H}_5$, is prepared by refluxing for

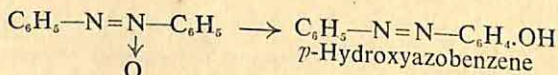
several hours nitrobenzene with sodium dissolved in large excess of methyl alcohol. On distilling off the alcohol from water-bath, azoxybenzene is obtained as an oil which solidifies on cooling. It is purified by re-crystallisation from petroleum ether. Sodium arsenite or aqueous glucose in presence of alkali may also be used for reduction.



Alkaline reducing agents convert nitrobenzene to nitrosobenzene which, on further reduction, readily gives phenylhydroxylamine. These two condense, in presence of alkali, to form azoxybenzene.



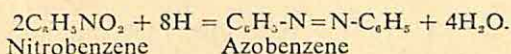
Azoxybenzene in good yield is also obtained by oxidising aniline with peracetic acid. It forms pale yellow needles (m.p. 36°), insoluble in water, but soluble in ether, alcohol and many other organic liquids. A second form, obtained by reduction of nitrosobenzene with aqueous-alcoholic caustic potash, melts at 84° . These are *cis-trans* isomers. On reduction, azoxybenzene first forms hydrazobenzene, $\text{C}_6\text{H}_5\text{-NH-NH-C}_6\text{H}_5$, and finally, aniline. In warm, conc. H_2SO_4 , by molecular rearrangement, *p*-hydroxyazobenzene, the parent substance of acid azo-dyes, results.



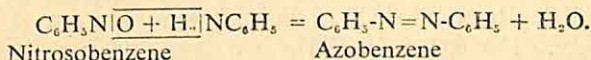
Since *p*-bromoazobenzene, $C_6H_4Br-N=N-C_6H_5$, on oxidation with hydrogen peroxide in presence of acetic acid, yields *two* isomeric monobromoazoxybenzenes, it is incorrect to represent azoxybenzene as $C_6H_5-N=N-C_6H_5$.

Azobenzene, $\text{C}_6\text{H}_5\text{-N=N-C}_6\text{H}_5$, is made by distilling azoxybenzene with three times its weight of iron filings. It is purified by recrystallisation from petroleum ether; azobenzene forms orange-red plates (m.p. 68°), freely soluble in alcohol and ether, but insoluble in water. It is more

conveniently obtained by reducing nitrobenzene with zinc dust and caustic soda, or an alkaline solution of stannous chloride (p. 347). Azobenzene exhibits *cis-trans* isomerism; the unstable *cis* form (m.p. 71°) is obtained from ordinary azobenzene in light petroleum in presence of ultra-violet light.

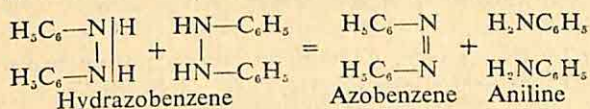


Nitrosobenzene in alcoholic solution reacts with aniline on warming and readily forms azobenzene (cf., formation of benzylideneaniline, p. 355).

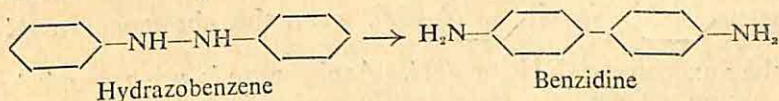


With alkaline reducing agents such as ammonium sulphide, or zinc dust and caustic soda, azobenzene forms hydrazobenzene, $\text{C}_6\text{H}_5\text{-NH-NH-C}_6\text{H}_5$. Acid reducing agents, e.g., zinc dust and acetic acid, SnCl_2 and HCl , etc., convert azobenzene into aniline. Azobenzene may be oxidised back to azoxybenzene with hydrogen peroxide in glacial acetic acid. Azobenzene is a coloured substance but *not* a dyestuff.

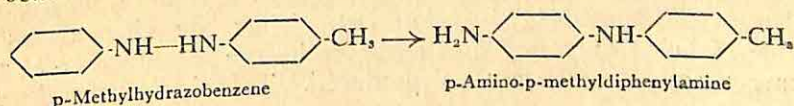
Hydrazobenzene, $\text{C}_6\text{H}_5\text{-NH-NH-C}_6\text{H}_5$, is prepared from azobenzene with alkaline reducing agents, or directly from nitrobenzene with zinc dust and hot aqueous caustic soda. The process is continued until the liquid becomes colourless. From the filtered solution, hydrazobenzene separates in *colourless* plates (m.p. 131° with decomposition). Mercuric oxide, sodium hypobromite or ferric chloride rapidly oxidises it to azobenzene; in air, it slowly turns orange due to oxidation to azobenzene. Acid reducing agents, e.g., SnCl_2 and HCl , or sodium amalgam readily converts it into aniline. On heating alone, it forms azobenzene and aniline—one molecule hydrogenates another:



When hydrazobenzene is slowly heated to boiling with moderately strong HCl , an intra-molecular change occurs, the benzene nuclei become turned, end for end, *pp'*-diaminodiphenyl or *benzidine* (as hydrochloride) is formed with a little *op'*-diaminodiphenyl. This remarkable change is known as *benzidine conversion* (cf., formation of *p*-aminoazobenzene, p. 370, and of *p*-toluidine, p. 362).



Hydrazo-compounds undergo this change if the *p*-positions are free. If, however, one has a substituent, a partial conversion, known as *semi-benzidine* or *semidine conversion*, occurs; e.g.,



Benzidine which has a demand for azo-dyes, is made in one stage from azobenzene with tin and *strong* HCl. Hydrazobenzene, first formed, undergoes benzidine conversion. Benzidine forms colourless crystals (m.p. 127°), practically insoluble in water; it dissolves in dilute HCl as the hydrochloride.

The azo-dyes.—A dye is a substance that can impart a coloration to a fabric by fixing itself to the latter so that the colour is not removed by washing with soap and water, or by friction. A coloured substance is not a dye unless it fulfils these conditions. Azobenzene is coloured, but cannot adhere to a fabric. A dyestuff may dye one type of fabric but not another. For example, picric acid dyes silk or wool a permanent yellow, but not cotton. Practically all dyestuffs are aromatic compounds; some 1500 are in use.

The relationship between *colour and constitution* is a fascinating topic in organic chemistry, but cannot be fully discussed here. From a study of many coloured compounds, it has been discovered that certain groups are responsible for the colour. These are called *chromophores* (*chroma* colour, *phoros* bearer) or colour-bearing groups by O.N. Witt (1876). The most important chromophores (which are usually unsaturated) are $-\text{NO}_2$, $-\text{N}=\text{N}-$, $-\text{N}=\text{O}$, $>\text{C}=\text{S}$, $>\text{C}=\text{C}<$, $=\langle \text{C}=\text{C} \rangle=$, etc.

Azobenzene, $\text{C}_6\text{H}_5-\text{N}=\text{N}-\text{C}_6\text{H}_5$, is coloured because it contains the chromophore, $-\text{N}=\text{N}-$; hydrazobenzene, $\text{C}_6\text{H}_5-\text{NH}-\text{NH}-\text{C}_6\text{H}_5$, is colourless as it has none. Benzene apparently containing three chromophoric groups ($>\text{C}=\text{C}<$) is colourless. A compound with a chromophore, coloured or not, is called a *chromogen*. Azobenzene is a chromogen. For a chromogen to function as a dye, certain other groups are necessary. These are known as *auxochromes* (*auxo* increase, *chroma* colour) or colour-helping groups which only deepen the colour, but cannot impart colour by themselves. The most effective auxochromes are $-\text{NH}_2$ and phenolic $-\text{OH}$; others are $-\text{NHR}$, $-\text{NR}_2$, $-\text{COOH}$, $-\text{HSO}_3$, etc. Auxochromes are either acidic or basic and are, therefore, salt-forming. They confer affinity for many fibres and make a dye *acidic* or *basic*. Azo-dyes are mostly sulphonic acids; so they are largely acid dyes. A dye should contain both a chromophore and an auxochrome, e.g., *p*-amino-azobenzene, $\langle \text{C}_6\text{H}_4 \rangle-\text{N}=\text{N}-\langle \text{C}_6\text{H}_4 \rangle\text{NH}_2$ and *p*-hydroxyazo-

benzene, $\langle \text{C}_6\text{H}_4 \rangle-\text{N}=\text{N}-\langle \text{C}_6\text{H}_4 \rangle-\text{OH}$, have the chromophore $-\text{N}=\text{N}-$ and the auxochrome $-\text{NH}_2$ or $-\text{OH}$. Azobenzene is not a dye, it has no auxochrome. Since dyes are generally applied in aqueous solution, they should be soluble in water. Many are sulphonated; the alkali salts of the sulphonic acids are readily soluble in water.

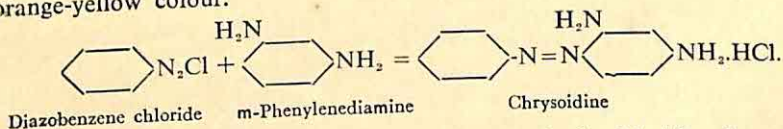
Aromatic azo-compounds having $-\text{N}=\text{N}-$ are all coloured (azomethane, $\text{CH}_3\text{N}=\text{NCH}_3$, is colourless). They are chromogens and capable of being converted into dyestuffs by the introduction of auxochromes; azo-colours are thus produced. This is usually done by

'coupling' them with amino- or phenolic bodies which contain auxochromes. The azo-dyes represent the largest group of synthetic dyes; their number almost equals the total of other dyestuffs. They colour wool, cotton and silk as also linen, paper, etc. They are obtained in any shade. Diazonium salts combine with primary or secondary aromatic amines to form diazoamino-compounds which are coloured (p. 370) but not dyestuffs, having no auxochromes. With tertiary 'mixed' aromatic-aliphatic amines or with phenols (compounds containing -OH group attached to the benzene ring), diazonium salts react to give *azo-dyes*. The reaction is technically called 'coupling'.

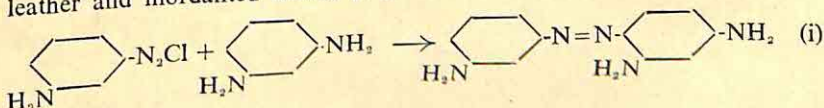
Production of azo-dyes.—The solution of a diazonium salt is cooled with ice, and slowly run into cold, *alkaline* solution of a phenol or its sulphonic acid. The reaction mixture should be slightly alkaline during coupling, as liberated hydrochloric acid hinders the process. The azo-dye is salted out with common salt, freed largely from water in a filter press, dried and ground. It is also sold as a paste. Coupling with aromatic amines is done likewise; a concentrated solution of the diazonium salt is added to the amine in slightly *acid* solution. Sometimes an alcoholic solution of the amine is used. During coupling, the azo-group, as a rule, enters the *p*-position with respect to the -OH, -NH₂ or substituted amino-group. If the *p*-position is occupied, it goes to the *o*-position. And if both *o*- and *p*-positions are substituted, no coupling takes place unless the azo group can displace the para-substituent; it never enters the meta-position. A diazonium salt can couple with aromatic amines and phenols containing diverse substituents—thus giving rise to a very large number of azo-dyes.

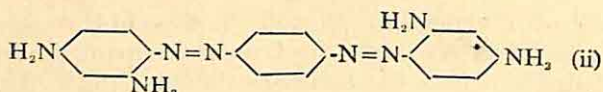
The simplest azo-dyes are yellow. On introducing alkyl or phenyl groups, and on increasing the mol. wt., their colour changes through orange and red to violet and blue. The best azo-dyes are made from naphthalene derivatives. The shade of the dyestuffs deepens with increase in the number of azo groups. A second or third azo-group may be introduced into the mol. of the mono-azo compound (coupled with a primary amine) by further diazotisation and coupling. The azo-dyes are sometimes made *in situ* i.e., on the fabric itself, by steeping it in an alkaline solution of the phenol, drying the fabric, and then passing it through a cold solution of the diazonium salt.

Chrysoidine, diaminoazobenzene, $C_6H_5-N=N-C_6H_4(NH_2)_2$, is made by coupling diazobenzene chloride with *m*-phenylenediamine in molecular proportions. The hydrochloride, an orange-red dye, is fairly soluble in water; it dyes silk and wool directly, and cotton soaked in tannin (mordanted) an orange-yellow colour.

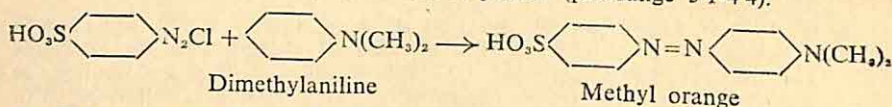


Bismarck brown is prepared by treating the hydrochloride of *m*-phenylenediamine with nitrous acid, one amino group of the diamine is diazotised, the diazo-compound then couples with the unchanged diamine, giving a brown azo-dye, triamino-azobenzene or *Bismarck brown*. Traces of nitrous acid or nitrite are thus detected and colorimetrically estimated in water-analysis. Bismarck brown is a mixture of hydrochlorides of (i) and (ii). The dye imparts to leather and mordanted cotton a dark brown colour.

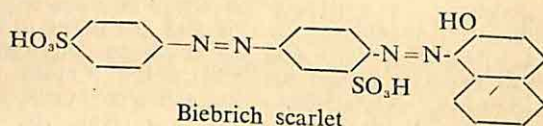




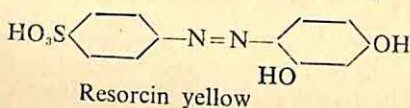
Methyl orange, dimethylaminoazobenzenesulphonic acid or helianthin is made by diazotising sulphanilic acid (aniline-*p*-sulphonic acid) with HCl and NaNO₂ in the usual way and coupling the diazonium compound formed with dimethylaniline hydrochloride. The sodium salt of the resulting azo-compound forms orange-yellow crystals and is known as *methyl orange*. It is fugitive and so seldom used as a dye; it is an indicator in volumetric analysis. The yellow colour of the aqueous solution is turned red by acids due to the unionised sulphonic acid which is red, the anion is yellow (pH range 3.1-4.4).



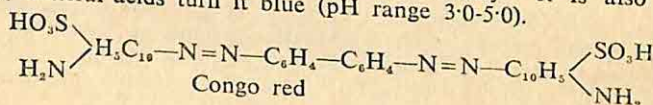
Biebrich scarlet is produced by diazotising aminoazobenzenedisulphonic acid (obtained by sulphonating aminoazobenzene) and coupling the resulting compound with β -naphthol in caustic soda. It is used in medicine; it dyes wool scarlet.



Resorcin yellow is made by diazotising sulphanilic acid and coupling the compound formed with resorcinol in caustic soda. The sodium salt is the dye, which is generally used mixed with other similar dyes.

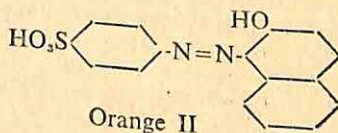
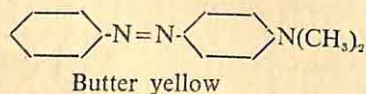


Congo red is prepared by diazotising benzidine and coupling with α -naphthionic acid. The sodium salt dyes cotton directly. It is also used as an indicator, mineral acids turn it blue (pH range 3.0-5.0).

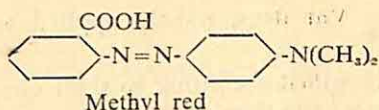


Congo red is a stronger acid than methyl orange. Only strong acids can change its colour. Congo red paper is sometimes used to distinguish between organic and mineral acids.

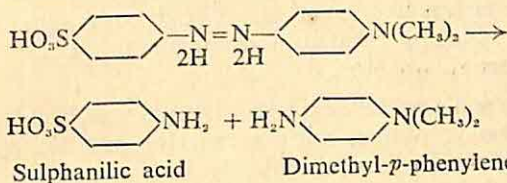
Butter yellow, *p*-dimethylaminoazobenzene, is a basic azo dye obtained by coupling diazobenzene chloride with dimethylaniline. It is insoluble in water and used to colour butter substitutes and oils. **Orange II**, a common azo dye, is made by diazotising sulphanilic acid and coupling the diazo-salt with β -naphthol.



Methyl red, an acid-base indicator, is made by coupling diazotised anthranilic acid with dimethylaniline in presence of hydrochloric acid. Acids colour it rose red, alkalis yellow.



With acid reducing agents (e.g., tin and HCl), an azo-dye molecule breaks at the double bond of --N=N-- , giving the original amine and the amino-derivative of the second component, used in coupling. Methyl orange thus decomposes into sulphanilic acid and dimethyl-*p*-phenylenediamine:



Dyeing.—Dyes are generally divided into four groups according to their mode of application:

(i) *Direct or substantive dyes* are applied by simply immersing the material in a hot aqueous solution of the dye; they attach themselves directly to it. Azo-dyes, as a rule, dye silk and wool directly and are, therefore, direct or substantive dyes for them. These, being protein fibres, are amphoteric (p. 305). They combine with acids as well as bases and so can be dyed directly by dyes having auxochromes, --NH_2 and --OH . The dye becomes insoluble due to chemical action. Materials to be dyed take up more dyes from the solution in presence of assistants such as sodium chloride, which reduce the solubility of the dye.

(ii) *Indirect, adjective or mordant dyes* fix themselves on the fabric in presence of mordants (*mordere* to bite) which are deposited on the material to be dyed beforehand. The dye and the mordant deposit an insoluble, coloured compound on the material. Iron, aluminium and chromium acetates (which deposit the oxide or hydroxide on subsequent steaming) are common mordants for acid dyes. Tannic acid is employed for basic dyes. For cotton and linen which are practically neutral, a mordant must be used with most azo-dyes which are, therefore, indirect for cotton. In both (i) and (ii) physical action due to surface adsorption plays an important role. Congo red is thus adsorbed by unmordanted cotton.

(iii) *Ingrain dyes* are developed by chemical action on fibres. An azo-dye can be formed on the material by dipping it in the alkaline solution of a phenol and then passing it through a solution of a diazo-salt (p. 375). Naphthol colours (or Brenthols) belong to this group. They are quite fast and applied to cellulosic fibres. Aniline black is deposited on the fibre likewise by oxidising aniline hydrochloride *in situ* with potassium chlorate.

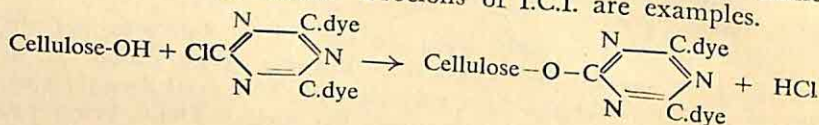
(iv) *Vat dyes* which are insoluble in water, are rendered soluble by alkaline reducing agents such as sodium hyposulphite. The fabric is dipped in this solution (which may not be coloured) and the original colour re-generated on the fibre by subsequent oxidation. This was formerly done in vats by fermentation, whence the name. Indigo is an

important vat dye. Vat dyes, mostly applied to cotton or linen, are quite fast.

Dyes are also classified according to their chemical constitution, *e.g.*, acid dyes, basic dyes, azo-dyes, sulphur dyes, triphenylmethane dyes, quinoline dyes, anthraquinone dyes, etc.

Sulphur dyes, containing sulphur, are soluble in aqueous sodium sulphide. They are applied to cotton and other vegetable fibres from this solution more or less like vat dyes. The dye is regenerated by oxidation with air or aqueous potassium dichromate. These are generally cheap and very fast to washing.

In recent years, a novel way of dye fixation has been introduced. A cationic dye is first combined with a reactive organic compound *e.g.*, cyanuric chloride, which then chemically combines with the alcoholic -OH groups of cellulose, forming an ether. Their exceptional fastness is due to this chemical union. 'Procions' of I.C.I. are examples.



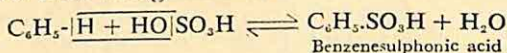
QUESTIONS

1. What products can be obtained by the reduction of nitrobenzene under different conditions? Give essential details and also equations. A.I.C. 1940.
2. Describe the preparation of methyl orange from sulphanilic acid. B.Sc., 1936, Punjab Uni.
3. How would you prepare azobenzene? What is the action of reducing agents upon it?
4. Starting from benzene, how could you obtain (i) azoxybenzene, (ii) azobenzene, (iii) amino-azobenzene and (iv) benzidine?
5. Classify the various dyestuffs. What is meant by an acid or a basic dye? What are mordants?
6. Discuss briefly the relationship between colour and constitution giving examples in support of your statements.
7. Give a short account of the substances which may be prepared from nitrobenzene by reducing it under various conditions. B.Sc. Degree Exam. 1941, Annamalai Uni.
8. Write short explanatory notes on (a) substantive dye, (b) chromophore, (c) auxochrome, (d) chromogen, (e) mordant, (f) lakes. Give examples. B.A. Degree Exam., 1941, Madras Uni.

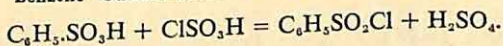
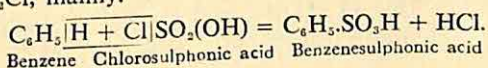
CHAPTER XXXVIII

THE SULPHONIC ACIDS

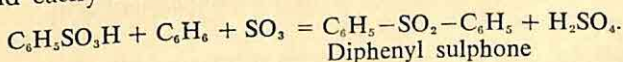
Aromatic hydrocarbons differ from the aliphatic in their behaviour towards conc. H_2SO_4 (p. 315). Benzene forms benzenesulphonic acid when heated with conc. H_2SO_4 , one of the H atoms being replaced by the sulphonic group, $-\text{SO}_3\text{H}$. Neutral SO_3 (present in pure H_2SO_4 or slightly aqueous H_2SO_4) rather than the cation, HSO_3^+ (formed by the ionisation of H_2SO_4) is now regarded as the active sulphonating agent. The process, known as *sulphonation*, is similar to nitration (p. 345). $-\text{OH}$ of the acid apparently combines with a hydrogen of benzene, water and benzenesulphonic acid being formed.



Aromatic compounds in general, e.g., hydrocarbons, amines, acids, phenols, etc. can thus be sulphonated with conc. H_2SO_4 . Chlorosulphonic acid in CCl_4 solution is also used; excess of this reagent gives benzenesulphonyl chloride, $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$, mainly.

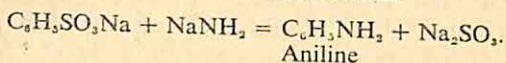
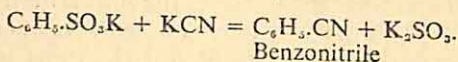
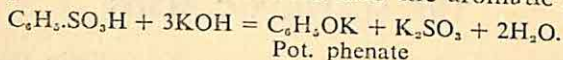


The number of $-\text{SO}_3\text{H}$ groups entering the nucleus depends upon the concentration of the acid, temperature and nature of the compound. Mercury, mercuric sulphate or iodine accelerates the process. In benzene, a maximum of three such groups can thus be introduced; benzene di- and trisulphonic (1:3:5) acids are obtained by heating benzene with *fuming* sulphuric acid to 200° and 300° respectively. The $-\text{SO}_3\text{H}$ group being meta-directing (p. 332), *m*-benzene-disulphonic acid is chiefly formed (together with some para-) on further sulphonation. $-\text{CH}_3$, $-\text{OH}$, $-\text{NH}_2$, etc. groups activate and $-\text{COOH}$, $-\text{NO}_2$ and $-\text{SO}_3\text{H}$ groups de-activate the benzene ring and make sulphonation easier or more difficult (p. 332). During sulphonation with fuming H_2SO_4 , a little *sulphone* results, which unlike sulphonic acid is insoluble in water and easily removed.

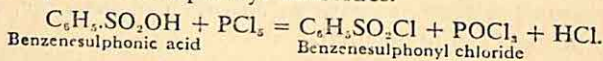


Properties.—The aromatic sulphonic acids are colourless, crystalline, highly soluble in water and generally hygroscopic. They are quite strong, being completely ionised in aqueous solution, and have a sour taste. Their salts including Ba, Ca and Pb salts are soluble in water; this enables us to separate them from sulphuric acid with baryta. Sulphonic acids are slowly hydrolysed by boiling water in excess but rapidly by conc. HCl under pressure at 150° . Benzenesulphonic acid thus yields benzene. These acids are relatively non-volatile; some, however, distil without decomposition at low pressures. Fused with

KOH, sulphonic acids give phenols (phenol is thus manufactured) and when distilled with KCN, aromatic nitriles are formed. Fusion of $C_6H_5SO_3Na$ with sodamide gives aniline. $-OH$, $-CN$ (and hence $-COOH$) groups can thus be introduced into the aromatic nucleus.

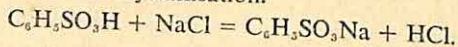


With phosphorus pentachloride, sulphonic acids or their anhydrous sodium salts produce sulphonyl chlorides.



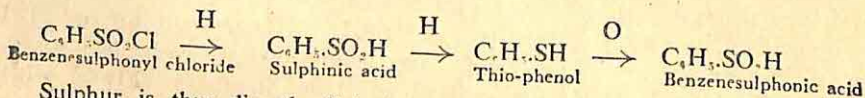
High solubility of sulphonic acids and their sodium salts is utilised in the dye industry. Many insoluble dyes are rendered water-soluble by sulphonation. Coal-tar benzene may be freed from thiophene with conc. H_2SO_4 ; thiophene is *more readily* sulphonated than benzene. The xylenes may be separated through sulphonation (p. 332). Sulphanilamide, $H_2N-C_6H_4-SO_2NH_2$ (1:4), and its substitution products such as sulphadiazine, sulphapyridine, etc. are excellent streptococides (p. 356).

Benzenesulphonic acid, $C_6H_5SO_3H$, is prepared by refluxing on a sand-bath, benzene (1 part) and conc. H_2SO_4 (2 parts) until all the benzene has dissolved. The mixture is cooled, poured into water and with powdered $BaCO_3$, unchanged sulphuric acid is precipitated as $BaSO_4$. On concentrating the filtrate, the barium salt crystallises. The free acid is liberated with conc. H_2SO_4 ; on evaporating the filtrate from a water-bath, benzenesulphonic acid crystallises in small, colourless, deliquescent plates with $1\frac{1}{2}$ mols. of H_2O (m.p. $43-44^\circ$); the anhydrous acid melts at 51° . $PbCO_3$ may replace $BaCO_3$. Lead is removed with H_2S to get the free acid. The sodium salt is prepared by pouring the acid into brine, sodium benzenesulphonate is salted out, or by adding Na_2CO_3 to the barium or lead salt until precipitation is complete; the filtered solution is concentrated to crystallisation.

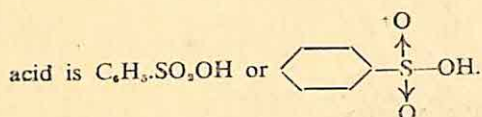


The acid ($k_a = 2 \times 10^{-1}$) is almost as strong as H_2SO_4 ; it is highly soluble in alcohol and water. Benzenesulphonic acid is difficult to esterify directly, but the acid chloride and alcohol readily give the ester in presence of caustic soda.

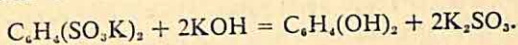
Constitution.—From analysis, benzenesulphonic acid is $C_6H_5SO_3$. The formation of monosubstituted benzenes such as benzonitrile, phenol, etc., from it shows that C_6H_5- is intact in benzenesulphonic acid, $C_6H_5(SO_3H)$. PCl_5 replaces an $-OH$ by a Cl atom, producing benzenesulphonyl chloride, $C_6H_5SO_2Cl$ (cf., formation of acetyl chloride from acetic acid, p. 152). Benzenesulphonyl chloride, when reduced with zinc dust and H_2SO_4 , first yields sulphinic acid and ultimately, thio-phenol or phenyl mercaptan; this, on oxidation, gives back the sulphonic acid.



Sulphur is thus directly linked to the nucleus. Hence benzenesulphonic

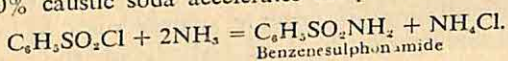


m-Benzenedisulphonic acid, $C_6H_4(SO_3H)_2$, is made by heating benzene with an excess of fuming H_2SO_4 at 200° ; a little *p*-isomer is also formed. On prolonged heating with conc. H_2SO_4 , the *m*-isomer is transformed into the *p*-. It resembles the monosulphonic acid. On fusion with potash, both isomers give *m*-dihydroxybenzene or resorcinol, $C_6H_2(OH)_3$.

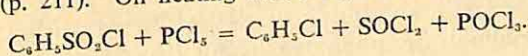


On sulphonation, toluene yields, more readily than benzene, *o*- and *p*-sulphonic acids which are used in making saccharin and chloramine T (a powerful antiseptic) respectively. Aniline forms mainly *p*-aminobenzenesulphonic acid or sulphanilic acid, $NH_2C_6H_4SO_3H$, which gives methyl orange (p. 376). Sulphanilic acid is also obtained from aniline sulphate (p. 356).

Benzenesulphonyl chloride, $C_6H_5SO_2Cl$, is prepared by heating benzenesulphonic acid (or its salt) with PCl_5 on water-bath, or from benzene and excess chlorosulphonic acid, $ClSO_3H$ (p. 379). It is an oily liquid (b.p. 251°), soluble in ether. The sulphonyl chlorides are fairly stable, they are only slowly decomposed by water (cf., acetyl chloride, p. 162). With strong ammonia, they form sulphonamides; these are crystalline, have definite m.p., and so help the identification of sulphonic acids. With primary and secondary amines (aliphatic or aromatic) but not with the tertiary, they combine giving substituted sulphonamides, of which only those from primary amines are soluble in alkali. Hence they can be separated. Benzenesulphonyl chloride forms esters with alcohols, 10% caustic soda accelerates the process.



Benzenesulphonyl chloride is employed in Hinsberg's method for the separation of amines (p. 211). On heating with PCl_5 , it forms chlorobenzene:



QUESTIONS

1. How is benzenesulphonic acid prepared? Show in outline how you can synthesise four different types of compounds from this substance. B.A. Degree Exam., 1942, Madras Uni.
2. How are aromatic sulphonic acids prepared? How are they obtained in free state? Give synthetic use of sulphonic acids in replacing H of benzene by OH, CN and Cl. Do you know any technical use of sulphonic acid? B.Sc. 1945, Nagpur Uni.
3. What useful purposes are served by sulphonation? Give concrete examples.
4. How is benzenesulphonyl chloride prepared? What are its uses? How does it react with ammonia, amines, and PCl_5 ? Give equations.
5. Describe some of the properties of benzenesulphonic acid. Explain how benzene, chlorobenzene, phenol and phenyl cyanide may be obtained from it. B.A. & B.Sc. Pass, 1932, Allahabad Uni.

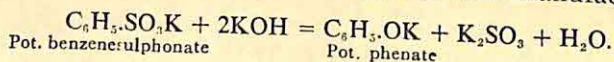
CHAPTER XXXIX

THE PHENOLS

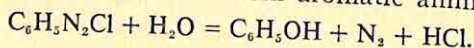
If one or more hydrogen atoms of benzene be replaced by hydroxyl groups, we get *phenols*. They are mono-, di- or trihydric, etc., according to the number of -OH groups entering the nucleus. Thus carbolic acid, C_6H_5OH , is a monohydric, catechol, $C_6H_4(OH)_2$, a dihydric and phloroglucinol, $C_6H_3(OH)_3$, a trihydric phenol. All the hydrogen of benzene may be substituted by -OH groups; hexahydroxy-benzene, $C_6(OH)_6$, is a white solid, sparingly soluble in cold water. Apparently, the phenols are analogous to aliphatic alcohols. Structurally, however, they are similar to aliphatic enols (p. 198). Their names end in 'ol', e.g., cresol, catechol, phloroglucinol, naphthol, etc. (cf., methanol, ethanol, etc.). They bear some resemblance to alcohols, no doubt, but differ from the latter in other respects. Phenols, for example, are weak acids, forming salts with bases while aliphatic alcohols are neutral. Ordinary phenol, C_6H_5OH , is called *carbolic acid*. Aromatic hydroxy-compounds with -OH in the side-chain are the alcohols e.g., benzyl alcohol, $C_6H_5.CH_2OH$. They are neutral and resemble aliphatic alcohols in their mode of formation and properties (*vide* Chapter XL).

Preparation.—(i) *From coal-tar*: Some phenols are formed during the destructive distillation of organic matter such as wood and coal. Coal- and wood-tar contain a few. Much of the carbolic acid of commerce comes from coal-tar. Phenol and cresols (hydroxytoluenes) occur together in the 'middle oil' fraction of coal-tar distillation. These are dissolved in dilute NaOH and free phenols liberated by H_2SO_4 followed by fractional distillation.

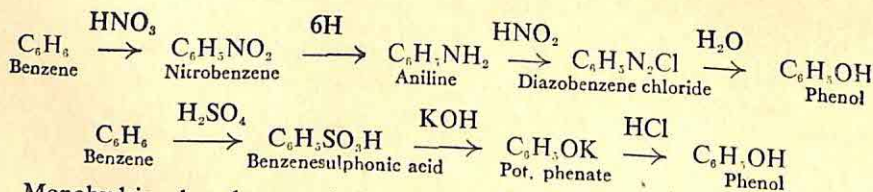
(ii) When aromatic sulphonic acids are fused with caustic alkalis, alkali salts of phenol or phenates result (p. 380). These give free phenols with dilute acids. Carbolic acid is thus manufactured.



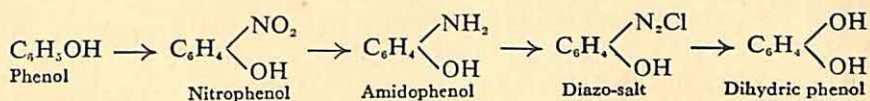
(iii) On boiling with water, diazonium salts yield phenols (p. 367). They may, therefore, be obtained from aromatic amines.



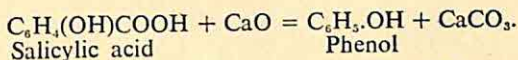
Methods (ii) and (iii) indirectly suggest the way of obtaining phenols from hydrocarbons:



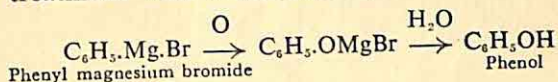
Monohydric phenols may similarly be converted into dihydric phenols:



(iv) Phenols result when phenolic acids are distilled with soda-lime (*cf.*, formation of benzene from sodium benzoate, p. 320).



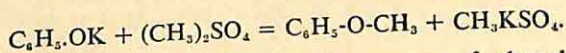
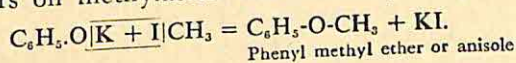
(v) Aromatic organo-metallic compounds (Grignard reagent) in ethereal solution produce phenols by the action of dry oxygen, and subsequent treatment with dilute mineral acids.



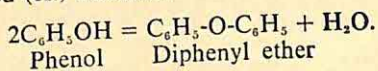
Phenols are not ordinarily formed on treating aryl halides with aqueous alkalis (*cf.*, formation of alcohols from alkyl halides, p. 74). But chlorobenzene, heated under pressure with aqueous caustic soda in presence of copper salts, yields phenol.

Properties.—Phenols are colourless, crystalline solids with low melting points. All are volatile in steam, many distil unchanged. They are soluble in alcohol and ether, but only sparingly soluble in water. The solubility in water generally increases with the number of -OH groups in the molecule; thus phenol, $\text{C}_6\text{H}_5\text{OH}$, is slightly soluble but pyrogallol, $\text{C}_6\text{H}_3(\text{OH})_3$, is highly soluble. $\text{C}_6(\text{OH})_6$ is, however, an exception. With the same number of -OH groups, the solubility falls with the increase in size of the hydrocarbon radical; menthol, $\text{C}_{10}\text{H}_{19}\text{OH}$, is practically insoluble in water. Most phenols possess a characteristic odour, and all have antiseptic property. Phenols contain the tertiary alcoholic group, $\equiv\text{C}\cdot\text{OH}$, and so resemble, to some extent, the aliphatic alcohols in their behaviour.

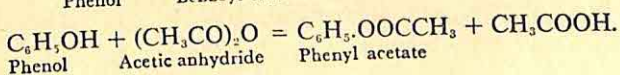
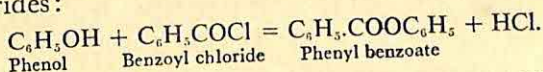
Reactions.—(1) Alkali phenates and alkyl iodides produce phenol ethers (*cf.*, formation of ether from $\text{C}_2\text{H}_5\text{ONa}$, p. 120). Phenols easily give methyl ethers on methylation with dimethyl sulphate and alkali.



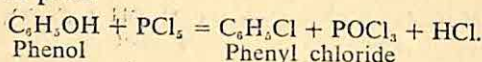
Phenol ethers are manufactured by passing vapour of phenol and alcohol over thoria at about 400° . When phenol vapour is led over fused zinc chloride, diphenyl ether is formed (*cf.*, formation of ethers from alcohols, p. 118).



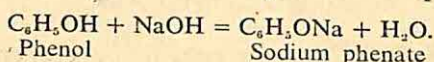
(2) Like alcohols, phenols yield phenyl esters with acid chlorides and acid anhydrides:



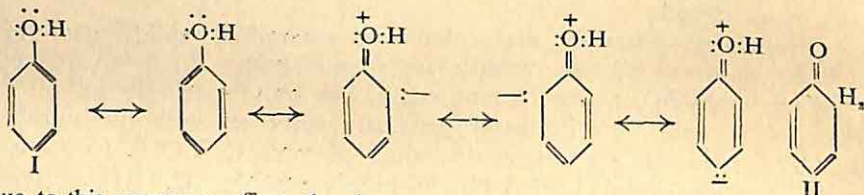
(3) Phosphorus pentachloride replaces the -OH group of phenols as of alcohols (but less readily) by chlorine; the products, unlike alkyl chlorides, are not hydrolysed by boiling alkalis. The phosphorus oxychloride formed reacts with unchanged phenol to give esters of phosphoric acid e.g., triphenyl phosphate, $\text{PO}(\text{OC}_6\text{H}_5)_3$; the yield of aryl halide is thus poor.



In the following reactions, phenols differ from alcohols: (i) Phenols react with alkalis forming salts called *phenates* or *phenolates*.

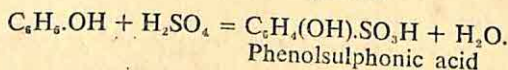
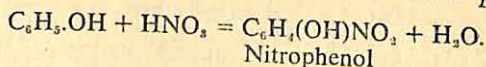


The acid character of phenols may be explained by the resonance theory; phenol, for example, exists as resonance hybrid. The enol form (I) is much more stable due to its high resonance energy (47.7 kcal. per mole) than the probable keto form (II).



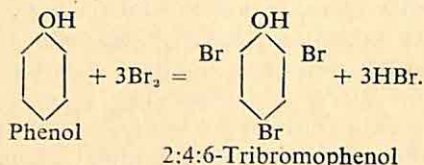
Due to this resonance effect, the electron density on the oxygen atom decreases, which consequently tends to assume a positive charge and pulls the pair of electrons between oxygen and hydrogen of the -OH group. This facilitates the escape of a proton. Such resonance is not possible in alcohols; the H of -OH, being more firmly bound than in phenols, cannot escape as proton. Alcohols are, therefore, neutral. An electro-negative group such as -NO₂ in the benzene ring tends to attract electrons away from the oxygen, the release of a proton (or the ionisation of phenol) is further facilitated. Nitrophenols are, therefore, stronger acids than phenol (k_a for *o*-nitrophenol is 6.5×10^{-8}); 2,4-dinitrophenol has $k_a = 1.0 \times 10^{-4}$, and trinitrophenol is a still stronger acid ($k_a = 4.2 \times 10^{-11}$) than nitrophenols. Phenols are extremely weak acids, so much so, that even carbonic acid decomposes their salts and sets free the phenols. k_a for carbonic acid is 1.3×10^{-10} at 25°, for carbonic acid, 3×10^{-7} at 18° and for water, 1.8×10^{-16} . This is utilised in separating phenols from carboxylic acids. The mixture is treated with NaOH and the aqueous solution of the sodium salts is saturated with CO₂; phenols are thus set free and removed by steam distillation.

(ii) Nitric and sulphuric acids form no esters with phenols, but give the corresponding nitro- and sulphonated products at ordinary temperature. Even dilute nitric acid produces *o*- and *p*-nitrophenols:

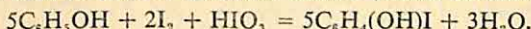


(iii) The -OH group, facilitates the substitution of other H-atoms of the nucleus. Phenol is more readily nitrated or halogenated than

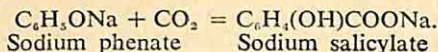
benzene. Bromine-water and phenol yield tribromophenol quantitatively. In non-ionising solvents *e.g.*, carbon disulphide or carbon tetrachloride, *o*- and *p*-bromophenols are formed.



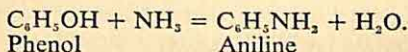
o- and *p*-iodophenol, $\text{C}_6\text{H}_4\text{IOH}$, can be obtained by adding a mixture of iodine and iodic acid to phenol in dilute caustic potash solution:



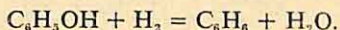
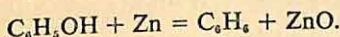
(iv) The alkali salts of phenols form hydroxy-carboxylic acids with carbon dioxide under pressure and at high temperature (*Kolbe's reaction*). Salicylic acid is thus manufactured from phenol.



(v) Phenols react with the double compound of calcium or zinc chloride and ammonia when heated, aromatic amines are mainly formed. Naphthylamines (q.v.) are thus technically made from naphthols. Heated with ammonia under pressure, phenol yields aniline.



(vi) They are reduced to hydrocarbons on distillation with zinc dust; carbolic acid thus gives benzene. Hydrogen in presence of molybdenum oxide at room temperature also yields benzene.



(vii) Phenols are susceptible to oxidation. Some of them, *e.g.*, pyrogallol in alkaline solution, readily absorb oxygen from the air and are converted into complex dark-coloured substances. This is utilised in gas analysis. Dihydric phenols (*o*- & *p*-) are oxidised to diketones called quinones (q.v.).

(viii) They couple with diazonium salts in alkaline solution forming azo dyes (p. 368).

(ix) Like nitroso-compounds, phenols respond to *Liebermann's reaction* (p. 363).

A little phenol is added to NaNO_2 solution in conc. H_2SO_4 and warmed gently. A brown or red colour, first formed, rapidly changes to deep blue or green. On dilution with much water, it turns red but on adding excess of NaOH solution, it again turns blue or green.

(x) Most phenols produce characteristic colorations—red, blue, violet, brown or green—with neutral or weakly acid ferric chloride solution. This helps their identification.

Ferric chloride gives coloration or coloured precipitate with compounds having the >C-OH group; *e.g.*, aceto-acetic ester, acetic acid, etc. Nitro-

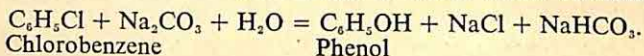
phenols or *m*- and *p*-hydroxybenzoic acids, however, give no colour with ferric chloride.

The monohydric phenols.—The most important and common is monohydroxybenzene, simply called phenol (*cf.*, alcohol and ether). Hydroxytoluenes or cresols, $C_6H_4(CH_3)OH$, come next.

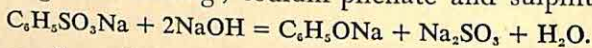
Phenol, C_6H_5OH , was discovered in coal-tar in 1834 by Runge who named it 'carbolic acid' (*carbo* coal, *oleum* oil), by which it is popularly known. One commercial source is coal-tar; some phenol is also obtained in the purification of ammoniacal liquors in coke and gas plants. It occurs in our urine as its hydrogen sulphate.

Preparation.—(1) The middle oil fraction (boiling range 170° - 230°) contains about 25-40% of phenol and cresols, mixed with naphthalene, a little toluene, xylenes, etc. This is subjected to a further fractionation, and the portion coming between 170° - 205° contains most of the carbolic acid and naphthalene. On cooling, naphthalene mostly crystallises and is removed by centrifuging. The mother liquor is washed with dilute H_2SO_4 to remove the basic substances and treated with sufficient (10%) NaOH solution, while agitating by a current of air. The phenols dissolve but not the hydrocarbons. The alkaline liquid is drawn off, and acidified with sulphuric acid or treated with CO_2 under pressure. Phenols, thus set free, form a dark-coloured, oily layer. This is washed thoroughly with water and distilled. The distillate (crude commercial phenol) is fractionated, the portion boiling at 181° - 182° is almost pure carbolic acid. On cooling, phenol separates in colourless crystals which are removed from the still liquid cresols. About 1.5 lb. of phenol is obtained per ton of coal.

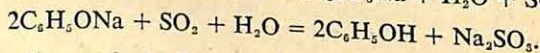
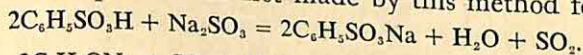
(2) When chlorobenzene and 10% aqueous soda ash under 200 atmospheres pressure are passed through copper-lined iron tubes at 320° (copper acts as a catalyst) phenol results (Dow process). The conversion is almost 100%. Some diphenyl ether, $C_6H_5.O.C_6H_5$, is also formed; the addition of 10% diphenyl ether to the reaction mixture prevents its formation. Chlorobenzene is made from benzene.



(3) Phenol is also made by the sulphonation of benzene followed by alkali fusion (p. 382). Sodium benzenemonosulphonate (1 mole) is added to 80% caustic soda (3 moles) in a nickel or iron pot at 320° - 350° with vigorous stirring; sodium phenate and sulphite are formed:

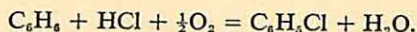


The reaction mixture is cooled and treated with just sufficient water to dissolve the phenate only; the sulphite remains mostly undissolved, it is employed for making sodium benzene-sulphonate from the sulphonic acid, and sulphur dioxide to liberate the phenol. During the war of 1914-18, phenol was first made by this method for picric acid.

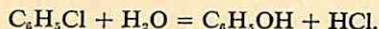


(4) **Raschig method**, discovered in Germany and followed in U.S.A. since 1940, is carried out in two stages:

(i) Benzene is chlorinated in vapour phase with hydrogen chloride and air under pressure at about 230° in presence of Cu-Fe catalyst on alumina. The chlorine comes from the decomposition of HCl by air in presence of cupric chloride. The conversion is about 10%; chlorobenzene is separated by fractional distillation.



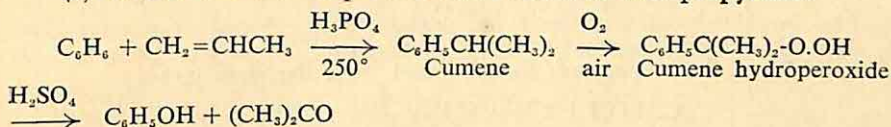
(ii) Chlorobenzene is hydrolysed at about 425° with silica catalyst:



The conversion is about 10%. The HCl is re-used. Pure phenol is thus obtained. Diphenyl oxide and other bye-products are less than 0.1%. The process is economic; ultimately air and benzene give phenol:



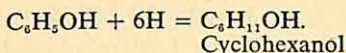
(5) U.S.A. now makes phenol from benzene and propylene:



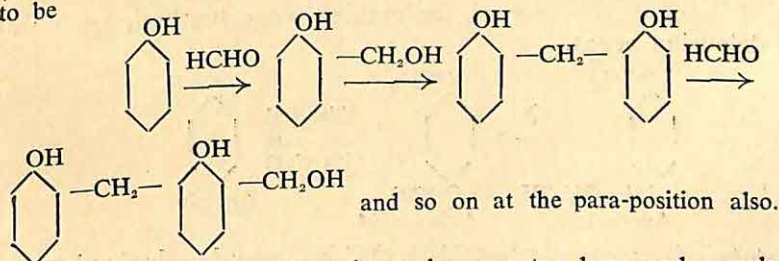
Properties.—Phenol forms large, colourless, deliquescent prisms (m.p. 42°, b.p. 181°). It has a strong, characteristic odour by which it may be recognised. It is soluble in alcohol or ether, and slightly in water (1 in 15 parts of water at 20°). But above 67° it is completely miscible with water. Phenol is a poison; it coagulates proteins; in fairly large dose, it causes death. It is a common antiseptic and disinfectant, but some bacteria thrive well in phenol. It is corrosive and so not an ideal antiseptic. Its general reactions have been mentioned on pp. 383-85; the following are also important.

(i) In air and light, phenol slowly suffers oxidation and turns pink. KMnO_4 breaks it up into oxalic and *meso*-tartaric acid. KClO_3 and HCl give chloroquinone or *chloranil*, $\text{C}_6\text{Cl}_4\text{O}_2$.

(ii) Hydrogenated in presence of finely divided nickel at 160°-170°, phenol produces cyclohexanol or hexahydrophenol (p. 313), an industrial solvent; adipic acid for Nylon is obtained from this (p. 245).



(iii) Heated with formalin in presence of an acid or alkaline catalyst, it forms a plastic, called *Bakelite* after its discoverer L. H. Bakeland of America (1908). The condensation process is complex; the initial steps are believed to be

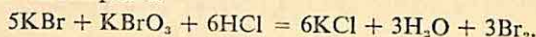


This continues until the polymer becomes too large and complex to crystallise, and forms resins. Bakelite is extensively used in making electrical fittings, artificial amber, ivory, etc. Synthetic processes for phenol have been developed mainly to meet its extraordinary demand for plastics. The largest group of plastics are made from phenol and aldehydes (phenolics). These may be moulded, laminated or cast.

Tests.—(i) Phenol gives a violet coloration with neutral aqueous FeCl_3 . (ii) It gives Liebermann's test (p. 385). (iii) On adding bromine-water to an aqueous solution of phenol, a white ppt. of tribromophenol is obtained.

(iv) Warmed with ammonia and a few drops of sodium hypochlorite solution, phenol produces a blue colour. (v) Solid phenol (0.5 g.), phthalic anhydride (0.5 g.) and strong H_2SO_4 (2 drops) are fused together, cooled and then made alkaline with NaOH —a pink coloration, due to phenolphthalein, appears.

Estimation of phenol.—A bromide-bromate (5:1) mixture in water is standardised by adding pot. iodide and dilute H_2SO_4 and titrating the iodine with deci-normal thiosulphate.



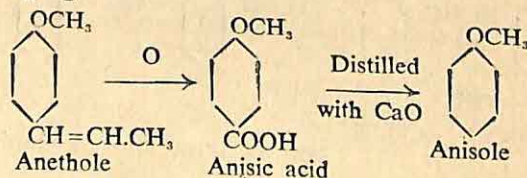
The bromide-bromate solution in presence of a mineral acid precipitates the phenol quantitatively as 2:4:6-tribromophenol. Excess of bromine is determined and the amount of phenol found from the equation:



Uses.—Phenol is a common antiseptic and disinfectant, used as carbolic soaps, lotions, etc. A 3% solution is generally employed for washing wounds. Bakelite, picric acid, amidophenols (photo-developers), salicylic acid, phenacetin, phenolphthalein, some dye intermediates, synthetic tannins, etc. are made from phenol. It is hydrogenated to cyclohexanol, a solvent for rubber and nitrocellulose lacquers. Cyclohexanol is oxidised to adipic acid for making Nylon. Pentachlorophenol, $\text{C}_6(\text{OH})\text{Cl}_5$, obtained by chlorinating phenol in presence of a halogen carrier, is an effective wood preservative and fungicide.

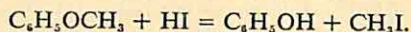
In 1955-56 India imported 8.019 cwt. of phenol valued at Rs. 7,70,120, her annual demand is 1,200 tons. U.S.A. made 517 million lb. of phenol in 1955, 475 million lb. being synthetic.

Phenol ethers.—The preparation of phenol ethers has already been mentioned (p. 383). Anisole or phenylmethyl ether, $\text{C}_6\text{H}_5\text{OCH}_3$, is made by methylating phenol with dimethyl sulphate and caustic soda. It is obtained in good yield when phenol and methanol vapours are passed over alumina at about 400° . Anethole of oil of aniseed is oxidised to anisic acid which, on distillation with lime, yields anisole. It is a colourless liquid (b.p. 155°) with a fragrant smell, insoluble in water. It is used as a solvent, for making some synthetic perfumes and as a delousing agent.



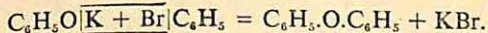
Phenetole, phenylethyl ether, $\text{C}_6\text{H}_5\text{O.C}_2\text{H}_5$, may be obtained from potassium phenate and ethyl iodide. It is a pleasant-smelling liquid (b.p. 172°). Anisole and phenetole, being true ethers, are not hydrolysed by boiling caustic alkalis. Phenetole is the starting material for *p*-aminophenetole or *p*-phenetidine, $\text{C}_6\text{H}_4(\text{NH}_2)\text{OC}_2\text{H}_5$, required for azo dyes. *p*-Phenetyl carbamide, $\text{C}_2\text{H}_5\text{O.C}_6\text{H}_4.\text{NHCONH}_2$, is *Dulcin* (*dulcis* sweet) which is about 200 times as sweet as cane-sugar. It is made from phenetidine by reacting with carbonyl chloride and ammo-

nia. Phenol ethers are quantitatively decomposed by boiling conc. hydriodic acid. *Zeisel's method* for the detection and estimation of methoxy ($-\text{OCH}_3$) and ethoxy ($-\text{OC}_2\text{H}_5$) groups is based on this.



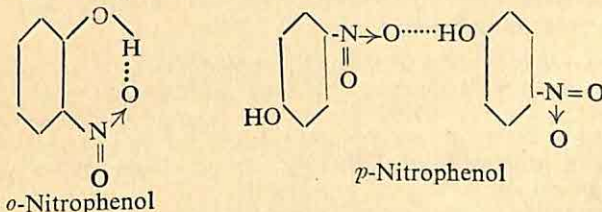
Zeisel's method.—The substance (0.2-0.4 g.) is heated to 130° - 140° with HI (15-20 c.c.) of sp. gr. 1.7, in a small round-bottomed, distilling flask with a long neck, on a glycerol- or oil-bath. It is connected to two conical flasks containing aqueous-alcoholic AgNO_3 . A slow stream of CO_2 sweeps the alkyl iodide formed from the distilling to conical flasks where AgI is formed (p. 75). This is boiled with HNO_3 , filtered, washed, dried and weighed. From the weight of AgI , that of alkyl iodide is known, and hence the p.c. of methoxy or ethoxy group in the compound. The number of such groups per mol. is found from the mol. wt. of the compound. The acid must not distil over to the conical flasks. Hydriodic acid of sp. gr. 1.70 has a constant b.p. 126° .

Diphenyl ether, $\text{C}_6\text{H}_5\text{O.C}_6\text{H}_5$, is formed by reacting phenol with zinc chloride (p. 383) and also as a bye-product in the manufacture of phenol from chlorobenzene (p. 386). Bromobenzene and potassium phenate react in presence of finely divided copper at 200° and yield diphenyl ether (m.p. 27° , b.p. 259°). It smells like geranium and is a perfume for soaps. Boiling HI cannot decompose it; for its stability at high temperature, it is a heat-transfer medium like diphenyl.

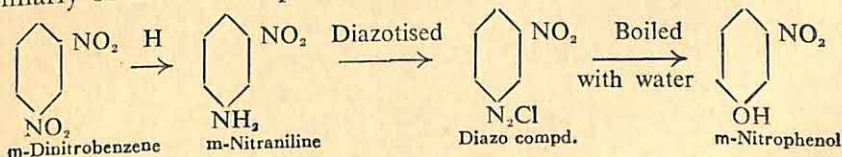


Diphenyl ether

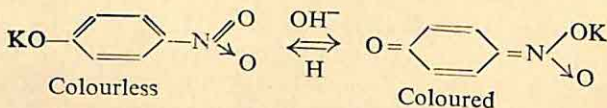
The nitrophenols.—*o*- and *p*-nitrophenols result on heating nitrobenzene with solid caustic potash. The $-\text{OH}$ group in phenols greatly facilitates their nitration by activating the benzene ring. Conc. HNO_3 converts phenols into dark resins. Phenol, with *dilute* HNO_3 in the cold, yields *o*- and *p*-nitrophenols. These are separated by steam distillation, the ortho-compound distils off leaving behind most of the much less volatile para-. The *p*-compound remains dissolved in the aqueous distillate, the *o*-compound is sparingly soluble in water, it has an internal hydrogen bond resulting in chelation unlike the other isomers which are associated by intermolecular hydrogen bonding. Its lower m.p. and greater volatility in steam are thus explained.



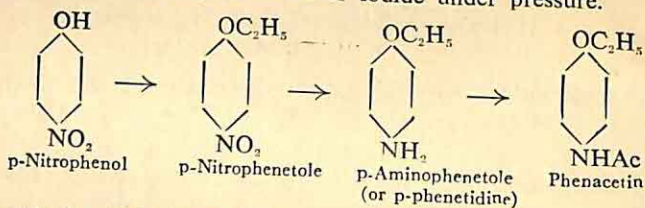
m-Nitrophenol is prepared from *m*-dinitrobenzene by reduction with ammonium sulphide, and diazo-reaction. *p*-Nitrophenol may be similarly obtained from *p*-nitroacetanilide.



Properties.— *o*- and *m*-nitrophenol are yellow, crystalline solid (m.p. 45° and 96° respectively). The *p*-compound (m.p. 114°) is colourless (but dissolves in alkalis with a deep yellow colour, hence its use as an indicator) and crystalline. *o*-Nitrophenol is volatile in steam. *p*- and *m*-isomers are fairly soluble in cold water. They are stronger acids than phenol due to the -NO_2 group (p. 384), they decompose carbonates. On reduction, they yield the corresponding amidophenols which are good photographic developers. During halogenation in aqueous medium, the nitro group generally splits off from *o*- and *p*-nitrophenols; thus on bromination, both yield 1:3:5-tribromophenol. The coloured salts (and ethers) of nitrophenols are believed to have the quinonoid structure (q.v.), the colour changes over pH 5-7.



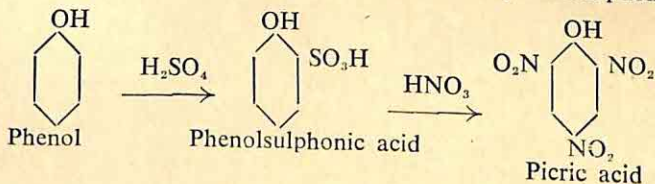
Phenacetin, *p*-acetaminophenetole is obtained from *p*-nitrophenol by ethylating and then reducing to the amino-compound, phenetidine; the latter, on acetylation, yields phenacetin. The ethylation is done by heating the sodium salt of nitrophenol with ethyl chloride or iodide under pressure.



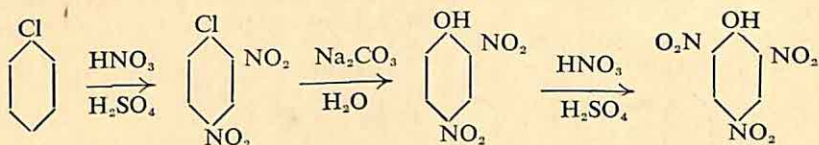
Phenacetin is chiefly used for headache and neuralgia together with aspirin and caffeine (A.P.C. powder). Phenetidine is highly toxic but on acetylation, basicity, to which its toxic character is due, is reduced and a useful drug results. Phenacetin is less toxic than acetanilide (p. 357).

Picric acid, 2:4:6-trinitrophenol, discovered by P. Woulfe of Woulfe's bottle fame, is the most important of nitrophenols. Wool, silk, leather, indigo, some resins, etc., turn yellow with conc. nitric acid due to the formation of picric acid.

Preparation.—Gently boil phenol (8 g.) and conc. H_2SO_4 (10 c.c.) in a flask. Cool the mixture in ice-cold water and carefully add to it water (10 c.c.) and conc. HNO_3 (30 c.c.) with shaking. This should be done in a fume-chamber. When no more brown fumes evolve, heat the mixture on water-bath for about 1½ hrs. with occasional shaking. Slowly pour the liquid into cold water (100 c.c.) and stir well; yellow crystals of picric acid separate. Filter, wash, and re-crystallise from aqueous alcohol (1 part alcohol in 2 parts water). Resinous by-products are formed from phenol due to oxidation and condensation if it is nitrated with nitric acid alone, but not from phenolsulphonic acid.



It is manufactured likewise and also from chlorobenzene :



Picric acid is a pale yellow, crystalline solid (m.p. 122°) having an extremely bitter taste (Greek *pikros* bitter). It is slightly soluble in cold, but fairly soluble in hot water; it readily dissolves in alcohol, ether and benzene. The aqueous solution is deep yellow due to the coloured ion, $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{O}^-$; the unionised solution in light petroleum is colourless. Three nitro groups have considerably strengthened its acid character ($k_a = 4.2 \times 10^{-1}$). It forms well-defined salts called *picrates*, and decomposes alkali metal carbonates. With PCl_5 , picric acid forms *picryl chloride*, $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{Cl}$, which, like acid chlorides, is hydrolysed back to picric acid, and with ammonia gives picramide or trinitro-aniline, $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{NH}_2$. Compounds with one, two or three amino groups result on reduction.

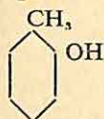
Picric acid may be regarded as the first synthetic dyestuff; it dyes directly silk and wool (but not cotton) a deep yellow colour which, however, is not very fast; it has only a limited use as a dyestuff. The acid explodes violently when detonated, and is a high explosive in shells, bombs and torpedoes (*lyddite* or *melinite*). Picrates (particularly lead picrate) are still more explosive. The acid is, however, quite safe to handle; it can even be slowly heated to decomposition. An aqueous solution (1%) of picric acid relieves pain due to burns, and cures certain skin diseases. It is poisonous. Picric acid forms crystalline addition compounds with many aromatic amines and hydrocarbons, as also with phenols, and thus helps in their identification. Naphthalene picrate (m.p. 149°) is yellow, anthracene picrate (m.p. 138°) is red, while benzene picrate (unstable) is colourless.

On distilling picric acid with bleaching powder and water, a colourless, heavy liquid (b.p. 112°) called nitrochloroform or *chloro-picrin*, CCl_3NO_2 , with a suffocating smell is obtained. It attacks the eyes and mucous membrane, and induces vomiting; it is an insecticide and was used in the war of 1914-18 as a *poison gas*. One part in a million of air causes copious flow of tears. It may also be obtained from chloroform and conc. nitric acid, or from nitromethane, hypochlorous acid and calcium carbonate. Potassium picrate is much less soluble than sodium picrate; this is useful in testing for potassium in presence of sodium.

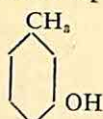
Test.—Aqueous solutions of picric acid and pot. cyanide, on warming together, give an orange-red colour due to the formation of isopurpuric acid.

The cresols, $\text{C}_6\text{H}_4(\text{CH}_3)\text{OH}$.—The three isomeric cresols (*o*-, *m*- and *p*-) or hydroxytoluenes, also called *creosote* or *cresylic acids*, occur together with phenol in the middle oil fraction of coal-tar distillation and in pine and beech wood-tar. *p*-Cresol is a decomposition product of some proteins, its sulphate occurs in urine. After the separation of

phenol (p. 386) the cresols remain in the mother-liquor. By further fractionation, *o*-cresol may be separated but not the meta- and para- which have practically the same b.p.

*o*-Cresol

(m.p. 31°, b.p. 190°)

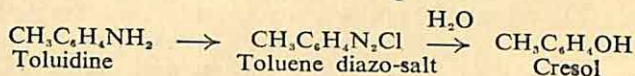
*m*-Cresol

(m.p. 4°, b.p. 202°)

*p*-Cresol

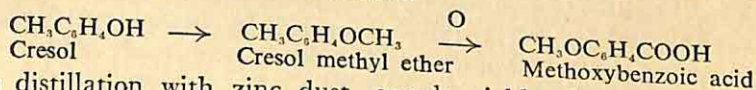
(m.p. 36°, b.p. 203°)

Cresols are obtained pure either by hydrolysing diazo-salts of toluene or by potash fusion of toluenesulphonic acids.



Properties.—Cresols are oily liquids having a peculiar phenolic odour. They closely resemble phenol but are less soluble in water. They are slightly weaker acids than phenol. Coal-tar cresols in which the meta-compound predominates, are not usually separated but rendered water-soluble by adding resin- or oil-soap. This is used as a disinfecting liquid under various trade names such as *lysol*, *creolin*, *phenyle*, etc. Cresols are cheaper, have stronger antiseptic properties and are also less toxic than phenol. The methyl group increases the bactericidal property; the longer the alkyl group, the greater the activity. *n*-Hexylphenol is about 500 times more effective than phenol.

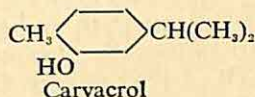
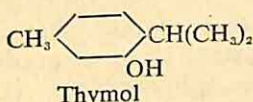
Neutral ferric chloride produces a blue coloration with cresols. Alkalis form salts which are decomposed by carbon dioxide. With chromic acid, cresols do not form hydroxy-acids (*cf.*, *o*-xylene, p. 333) but get decomposed. If, however, the -OH group is first methylated or acetylated, carboxylic acids are obtained.



On distillation with zinc dust, cresols yield toluene (*cf.*, phenol, p. 320). They are isomeric with anisole, $\text{C}_6\text{H}_5\text{OCH}_3$, from which they are readily distinguished by their solubility in caustic alkalis (acidic nature) and colour reaction with ferric chloride. Cresols are preservatives for wood (railway sleepers, for example). The condensation product of sulphonated cresols and formaldehyde is a synthetic tannin, *Syntan*. *Artificial amber*, made from cresols and formaldehyde, is a plastic of bakelite type, the cresol mixture being employed as such. Trinitro-*m*-cresol is an explosive; potassium salt of dinitro-*p*-cresol is the dye, *Victoria orange*. Tricresyl phosphate, $[\text{C}_6\text{H}_4(\text{CH}_3)_3\text{O}]_3\text{PO}$, made by heating cresols with phosphorus oxychloride, is an important plasticizer for cellulose acetate and nitrate; it forms a tough water-proof film and is used for coating cables.

Thymol or hydroxycymene is the chief constituent (about 40%) of oil of *thyme* (*Ajowan oil*), it is extracted therefrom with caustic soda and acidification with HCl. It forms colourless plates (m.p. 51.5°), sparingly soluble in water, and has the odour of oil of thyme. It gives no coloration with ferric chloride. On heating with phosphorus pentoxide, it forms *m*-cresol and propylene. Distilled with phosphorus pentasulphide, it gives *p*-cymene. Thymol is a mild antiseptic, often used in tooth-pastes. Its iodo-derivative, *aristol*, is a substitute for iodoform.

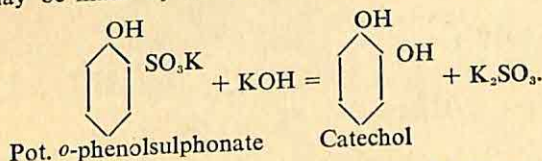
Carvacrol, an isomer of thymol, is present in the oil of *origanum hirtum*. It may be obtained by heating camphor with a little iodine. It is a liquid (b.p. 236°), which gives a green colour with alcoholic ferric chloride. On heating with phosphorus pentoxide, it forms *o*-cresol and propylene. Carvacrol is an antiseptic.



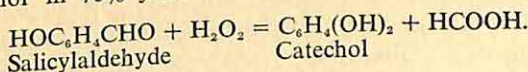
The dihydric phenols, dihydroxybenzenes (*o*-, *m*- and *p*-) are known as catechol, resorcinol and quinol respectively. They behave like the monohydric phenols but unlike the latter, possess reducing properties. The second phenolic -OH decreases the antiseptic activity considerably (resorcinol is only one third as active as phenol) but increases solubility in water. Catechol and resorcinol are stronger acids than phenol.

Catechol, pyrocatechol, *o*-dihydroxybenzene, $1,2\text{-C}_6\text{H}_4(\text{OH})_2$, occurs in the Indian *catechu* (obtained from the *Acacia catechu* tree) and was first obtained by dry distillation of this product, whence the name. Many resins, on alkali fusion, form catechol; so does lignin. In combined state, it is present in some natural tannins.

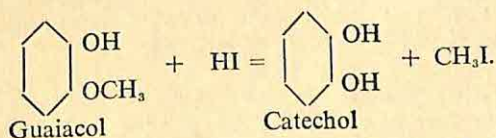
(i) It may be made by the potash fusion of *o*-phenolsulphonic acid:



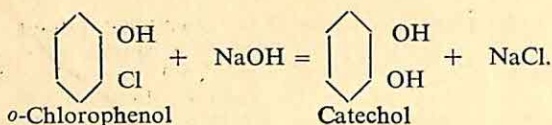
(ii) Oxidation of salicylaldehyde with alkaline hydrogen peroxide at about 50° , gives catechol in 70% yield (*Dakin reaction*):



(iii) Methylcatechol or guaiacol (present in beech-wood tar) when heated with hydriodic acid forms catechol (cf., Zeisel's method, p. 389). The demethylation may also be effected by 48% hydrobromic acid or aluminium chloride at 210° .



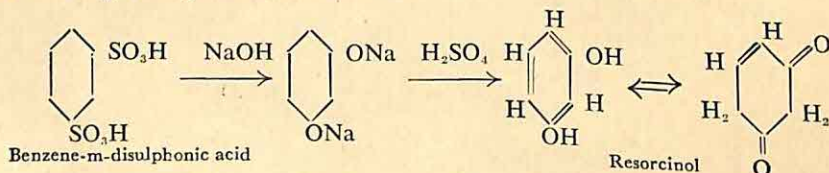
(iv) Catechol is commercially made by heating, under pressure to about 190° , *o*-chlorophenol or *o*-dichlorobenzene with 20% caustic soda in presence of a little copper sulphate:



Catechol is a colourless, crystalline solid (m.p. 104°), highly soluble in water. It sublimes readily and on exposure to air, gradually darkens. Alkaline catechol absorbs oxygen from the air. It gives a green coloration with ferric chloride solution, the colour changes to red on adding sodium bicarbonate solution. Other *o*-dihydric phenols behave likewise. Catechol reduces ammoniacal silver nitrate in the cold, and Fehling's solution, on warming, like an aldehyde. Silver oxide oxidises it in ether solution to *o*-benzoquinone (q.v.). Aqueous ammon. carbonate at 140° under pressure converts it to protocatechuic acid, $\text{C}_6\text{H}_3(\text{OH})_2\text{COOH}$ (1:2:4). Adrenalin, a valuable drug, is made from catechol.

Guaiacol, catechol monomethyl ether, $\text{C}_6\text{H}_4(\text{OH})\text{OCH}_3$, is a colourless, fragrant-smelling solid (m.p. 28°), obtained by fractional distillation of beech-wood tar. It was first made by distilling gum guaiacum. The carbonate is a good intestinal antiseptic. Guaiacol gives a green colour with ferric chloride.

Resorcinol, *m*-dihydroxybenzene, $\text{C}_6\text{H}_4(\text{OH})_2$, is made by fusing benzene-*m*-disulphonic acid with caustic soda at 270° for about eight hours. The mass is acidified and resorcinol extracted from the aqueous solution with ether or amyl alcohol. The *o*- and *p*-disulphonic acids of benzene, on potash fusion, also yield resorcinol, as one of the -OH groups migrates to the meta-position with respect to the other at the high temperature of fusion.

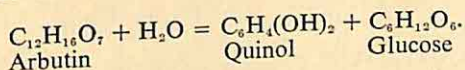


Resorcinol forms colourless needles (m.p. 110°), highly soluble in water, alcohol and ether. It gives a violet coloration with ferric chloride. Resorcinol very slowly reduces Fehling's solution and ammoniacal silver nitrate. Unlike catechol or quinol, it readily condenses with phthalic anhydride on heating and forms fluorescein which in dilute alkaline solution shows intense green fluorescence. Resorcinol forms a bisulphite compound and a dioxime like a ketone and also a diacetate and a diethyl ether as a hydroxy-compound; so it exists in tautomeric forms (cf., phloroglucinol, p. 396).

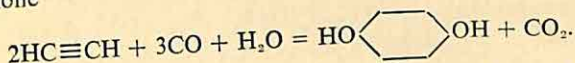
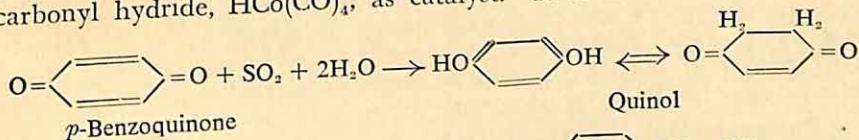
On heating with pot. bicarbonate solution, it readily forms potassium 2,4-dihydroxybenzoate $\text{C}_6\text{H}_3(\text{OH})_2\text{COOK}$. Resorcinol is largely used in making *fluorescein*, *eosin* and some azo dyes. With bromine-water, it gives crystalline tribromoresorcinol, $\text{C}_6\text{HBr}_3(\text{OH})_2$, (m.p. 112°). It is a remedy for eczema.

Orcinol, 3:5-dihydroxytoluene, $\text{CH}_3\text{C}_6\text{H}_3(\text{OH})_2$, a homologue of resorcinol, occurs in *orcina* and other lichens from which it is obtained. Orcinol (m.p. 290°) is a reagent for pentoses. Litmus, the common indicator, is prepared by treating these lichens with ammonia and potash and then fermenting the mass. The colouring matter of litmus is a derivative of orcinol.

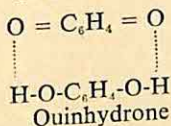
Quinol, *p*-dihydroxybenzene or hydroquinone, $\text{C}_6\text{H}_4(\text{OH})_2$, occurs as the glucoside *arbutin* in pear leaves; it may be obtained therefrom by acid hydrolysis or with *emulsin*.



It is prepared by reducing *p*-benzoquinone (made by oxidising aniline) with sulphurous acid and extracting the product with ether. Germany makes it from acetylene and carbon monoxide with cobalt carbonyl hydride, $\text{HCo}(\text{CO})_4$, as catalyst. It is tautomeric.

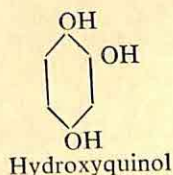
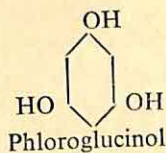
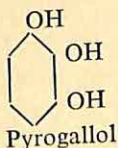


Quinol was first obtained by distilling quinic acid, hence the name. It is a colourless, crystalline solid (m.p. 169°), readily soluble in water, ethanol or ether but almost insoluble in benzene. The alkaline solution suffers autoxidation in air and turns dark. It is a strong reducing agent, and used as a photographic developer. Quinol, a powerful *anti-oxidant*, retards the oxidation of unsaturated oils by air. It gives a transient blue colour with ferric chloride which oxidises it to quinone on warming (*cf.*, catechol and resorcinol). Quinol and quinone form, possibly by hydrogen bonding at both ends, a green, crystalline, additive compound, *quinhydrone*, when the former is partially oxidised by ferric chloride in the cold. It is used in potential measurements.

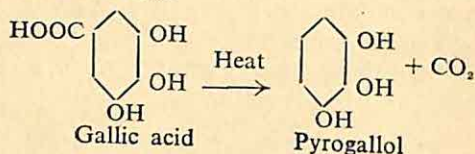


Unlike carbolic acid, the dihydric phenols have little corrosive action on the tissues. They may be distinguished by means of ferric chloride solution. From aqueous solution, lead acetate precipitates catechol but not the other two. None but catechol increases the electrical conductivity of boric acid (p. 278).

The trihydric phenols.—Benzene forms three trihydroxy-derivatives:

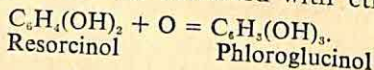


Pyrogallol, pyrogallic acid, $1,2,3\text{-C}_6\text{H}_3(\text{OH})_3$.—The gall nuts contain a solid acid called *gallic acid* which, on heating, gives pyrogallol. Scheele thus obtained pyrogallic acid in 1786. Pyrogallol-1-methyl ether occurs in beech-wood tar.

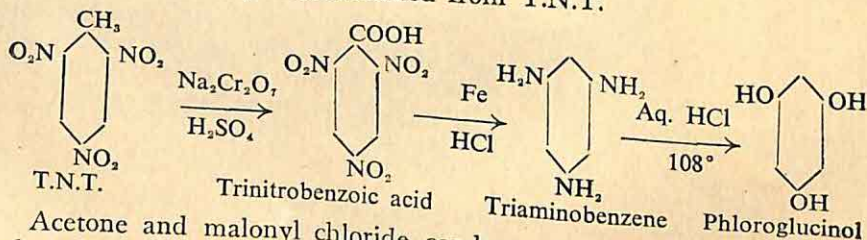


Pyrogallol is technically made by heating gallic acid to 175° with half its weight of water in an autoclave. It forms white needles (m.p. 132°), readily soluble in water but less so in alcohol and ether. It gives a red coloration with ferric chloride. The alkaline solution, when exposed to air, avidly takes up oxygen and turns dark-brown. It is, therefore, used for estimating oxygen in gas analysis. It liberates gold, silver and mercury from their salt solutions. For its strong reducing action, it is a common photographic developer. Pyrogallol is an antiseptic; some dyes are made from it.

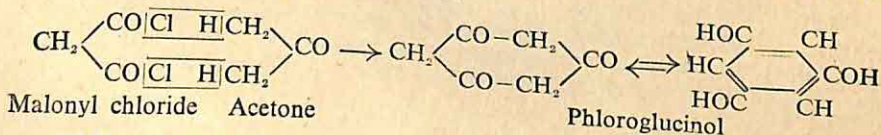
Phloroglucinol, $1,3,5\text{-C}_6\text{H}_3(\text{OH})_3$, occurs in the bark of apple trees as the glucoside, *phlorizin*, as well as in some resins and tannins. It is prepared by fusing resorcinol with six times its weight of caustic soda, resorcinol takes up an atom of oxygen from the air to give phloroglucinol. From the alkali salt formed, phloroglucinol is liberated by excess of dilute sulphuric acid and extracted with ether.



It is conveniently manufactured from T.N.T.



Acetone and malonyl chloride condense in presence of calcium carbonate and yield phloroglucinol:



Phloroglucinol forms colourless prisms with two mols. of water; the anhydrous compound melts and sublimes at 218° . It is highly soluble in water, alcohol and ether, and gives a bluish violet coloration with ferric chloride. It reduces Fehling's solution, absorbs oxygen in alkaline medium and turns brown. Acetyl chloride gives a triacetyl derivative, and diazomethane a trimethyl ether, showing three -OH groups. With hydroxylamine it also forms a tri-oxime, unlike pyro-

gallol or hydroxyquinol, indicating three keto groups. Hence it exists in tautomeric forms which, however, have not yet been separated.

Phloroglucinol in hydrochloric acid gives a pink coloration with pentoses on warming; with furfural (obtained from pentoses on distilling with 12% HCl) it forms an insoluble compound, used for estimating pentoses. Ligno-celluloses such as wood, jute, etc., give a cherry-red coloration with phloroglucinol. It is mainly used in photocopying.

Hydroxyquinol, 1,2,4- $C_6H_3(OH)_3$, results when quinol is fused in air with caustic potash. It melts at 140° , is highly soluble in water, and gives a greenish brown colour with ferric chloride. It is a strong reducing agent. In alkaline aqueous solution, it absorbs oxygen from the air like pyrogallol.

QUESTIONS

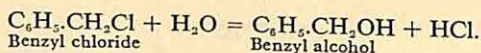
1. How is phenol isolated in pure state from coal-tar? What is Liebermann's test for phenols? Explain the principle underlying the process of steam distillation. B.Sc. Pass, 1940, Calcutta Uni.
2. How can you obtain (a) phenacetin, (b) phenetole, (c) catechol, (d) picric acid and (e) benzene from phenol?
3. What are the general methods for introducing a hydroxyl group into the benzene nucleus? In what important respects do they differ from aliphatic hydroxy compounds? B.Sc. Pass, 1942, Patna Uni.
4. A compound has the empirical formula C_7H_8O . What means would you adopt to assign it one of the three following possible constitutions— $CH_3C_6H_4OH$, $CH_3O-C_6H_5$, $C_6H_5CH_2OH$? B.Sc., London 1931.
5. How is phenol obtained from coal-tar, and what are its industrial applications? B.A. & B.Sc., 1937, Bombay Uni.
6. Compare and contrast the behaviour of ethyl alcohol and phenol, and mention the products obtained by the action of (a) chlorine, (b) nitric acid, and (c) sulphuric acid on each. B.A. & B.Sc. Pass, 1936. Allahabad Uni.; B.Sc. 1949, Gauhati Uni.
7. Indicate how you would distinguish, by (a) physical tests, and (b) chemical tests, between catechol and resorcinol. B.Sc., 1932, Punjab University.
8. State how you would proceed to introduce the hydroxyl group into a benzene ring. B.Sc. 1930, Punjab Uni.
9. What products are formed by the nitration of phenol? How may each of them be obtained in a pure condition? Discuss the effect of the introduction of nitro groups on the properties of the phenolic -OH. B.Sc. Degree Exam., 1942, Annamalai Uni.
10. Give the chemistry of (a) the dihydric phenols and (b) the phthalic acids. B.Sc. Degree Exam., 1941, Annamalai Uni.
11. How is phenol isolated from coal-tar? Mention its main physical and chemical properties. How could it be derived from benzene and be converted back into benzene? Determine the constitution of phenol, and state what is Liebermann's reaction. B.A. & B.Sc. Degree Exam., 1932, Andhra Uni.

CHAPTER XL

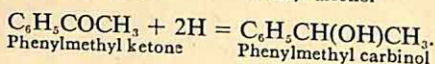
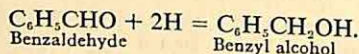
THE AROMATIC ALCOHOLS, ALDEHYDES, KETONES AND QUINONES

The aromatic alcohols.—If an -OH group enters the side-chain of an aromatic hydrocarbon, an aromatic alcohol results. The simplest is benzyl alcohol, $C_6H_5.CH_2OH$. In their general behaviour as well as mode of formation, they resemble the aliphatic alcohols and are classified as primary, secondary and tertiary likewise. They can be prepared:

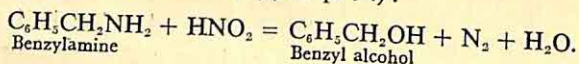
(i) By heating the corresponding halogen derivatives with water, alkalis or moist silver oxide (cf., method (1) in p. 93):



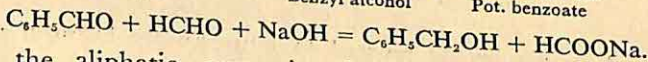
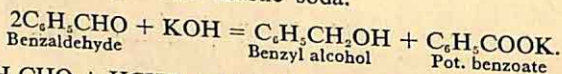
(ii) By reducing aromatic aldehydes or ketones with sodium amalgam (cf., method (3) in p. 94), hydrogen and a catalyst, or lithium aluminium hydride, $LiAlH_4$.



(iii) By the action of nitrous acid on primary aromatic amines having -NH₂ group in the side-chain (cf., method (4) in p. 94):



(iv) By the action of caustic potash solution on aromatic aldehydes, the corresponding alcohols are formed (Cannizzaro reaction, p. 130). Alcohols having the -CH₂OH group linked to the benzene nucleus can thus be made. Benzyl alcohol may also be obtained by 'crossed' Cannizzaro reaction from benzaldehyde, formaldehyde and caustic soda.

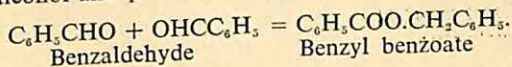


Like the aliphatic, aromatic alcohols form alcoholates, ethers, esters, aldehydes, ketones, acids, etc., under similar conditions. They are but aliphatic alcohols with a hydrogen of the alkyl group replaced by an aryl group; thus benzyl alcohol, $C_6H_5.CH_2OH$, is phenylmethyl alcohol or phenylcarbinol. Due to the presence of phenyl group, aromatic alcohols are less soluble in water (proportion of carbon to hydroxyl being higher) and have higher boiling points than aliphatic alcohols of corresponding molecular weight. The aromatic character is somewhat diminished by the side-chain; thus nitric acid does not nitrate benzyl alcohol but oxidises the side-chain and bromine enters the side-chain instead of the ring. Aromatic alcohols are esterified by concentrated halogen hydracids more readily than the aliphatic. They are neutral and insoluble in alkalis (cf., phenols).

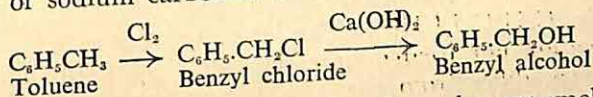
Benzyl alcohol, phenylcarbinol, $C_6H_5CH_2OH$, occurs free and as ester in many ethereal oils, e.g., jasmine oil contains the acetate. Tolu

and Peru balsams and storax (a resin) contain its benzoic and cinnamic acid esters. It is best prepared in the laboratory by Cannizzaro reaction mentioned above.

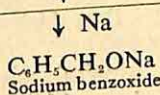
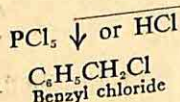
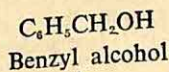
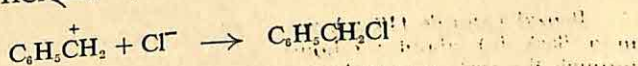
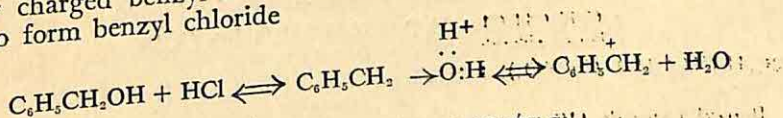
Preparation.—Benzaldehyde (30 c.c.) and a *strong* solution of caustic potash (25 g. in 20 c.c. of water) are shaken vigorously in a cork-stoppered, stout bottle until a permanent emulsion is obtained. It is allowed to stand overnight, sufficient water (100 c.c.) is then added to dissolve the potassium benzoate formed. The solution is extracted with ether, and on evaporating off the ether on water-bath, benzyl alcohol is obtained. It is purified by distillation. The unchanged aldehyde may be removed by shaking the ethereal solution with conc. sodium bisulphite solution before distillation. Two mols. of benzaldehyde probably polymerise to form benzyl benzoate which then suffers hydrolysis to give benzyl alcohol and potassium benzoate:



Most aromatic aldehydes having the -CHO group directly linked to the nucleus but not aliphatic aldehydes except formaldehyde give this reaction. Commercially, benzyl alcohol is made by boiling benzyl chloride (obtained from toluene, p. 342) with a mild alkali such as milk of lime or sodium carbonate solution.

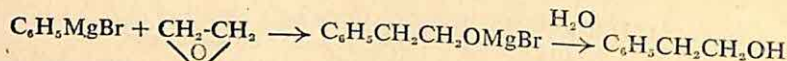
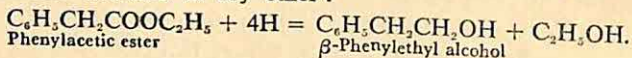


Properties.—Benzyl alcohol is a colourless, pleasant-smelling liquid (b.p. 206°, *d* 1.05), miscible with alcohol or ether, but having a small solubility in water. It has a burning taste. It is distinguishable from isomeric cresols as it is neutral, forms no salt with alkalis, gives no coloration with ferric chloride and has a non-phenolic odour. Benzyl alcohol yields esters with acids, benzaldehyde and benzoic acid on oxidation with nitric acid, benzoxide with sodium or potassium, benzyl chloride with phosphorus pentachloride and so on. It forms benzyl chloride with conc. HCl in the cold unlike aliphatic alcohols. H of HCl attaches itself to the O of OH and displaces an electron from the α-C atom towards the O; this weakens the C-O bond and facilitates removal of -OH. The resulting positively charged benzyl ion stabilises by resonance and readily adds a Cl- to form benzyl chloride



Benzyl alcohol is reduced to toluene by hydriodic acid in presence of phosphorus, sodium amalgam or lithium aluminium hydride. Conc. sulphuric acid forms no ester or ether but produces a resin; the aqueous acid converts it into dibenzyl ether, $(C_6H_5CH_2)_2O$. Benzyl alcohol has anæsthetic and antiseptic properties. It is used in ointments, the acetate and the benzoate are perfumes and also plasticizers in synthetic resin manufacture.

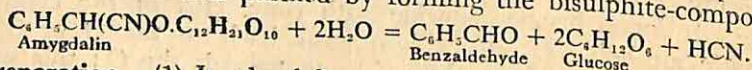
β -Phenylethyl alcohol, benzyl carbinol, $C_6H_5CH_2CH_2OH$, a colourless liquid (b.p. 220°) occurs in the essential oil (attar) of white rose (about 60%); it is a common perfume. It may be obtained by reducing phenylacetic ester with sodium and alcohol (*Bouveault-Blanc reaction*), or reacting ethylene oxide with phenyl magnesium bromide in dry ether:



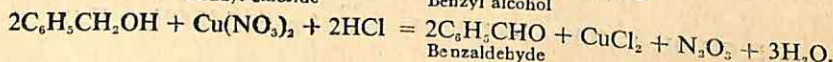
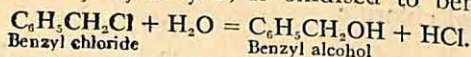
On heating with alkali, the alcohol dehydrates into styrene, $C_6H_5CH=CH_2$, which makes polystyrene plastics. γ -Phenylpropyl alcohol, $C_6H_5CH_2CH_2CH_2OH$, is used in blending perfumes.

The aromatic aldehydes have the $-CHO$ group in the nucleus (e.g., benzaldehyde, C_6H_5CHO) or in the side-chain (e.g., phenylacetaldehyde, $C_6H_5CH_2CHO$). The latter resemble the fatty aldehydes closely; they are not treated here separately. But the former, having no α -hydrogen, differ from the aliphatic in some respects. Benzaldehyde is a typical member of this group.

Benzaldehyde, oil of bitter almonds, C_6H_5CHO , occurs as a glucoside *amygdalin*, $C_{20}H_{27}NO_{11}$, in bitter almonds (*amygdale* almond), peach and cherry. In amygdalin, benzaldehyde cyanhydrin, $C_6H_5CH(OH)CN$, is coupled with gentiobiose, a disaccharide with two glucose units. It is hydrolysed on boiling with a dilute mineral acid, or by the enzyme *emulsin* (p. 214) present in the almond. Benzaldehyde is separated by steam distillation and purified by forming the bisulphite-compound.

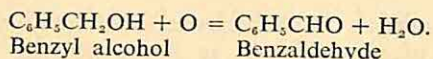


Preparation.—(1) In the laboratory, benzaldehyde is prepared by boiling benzyl chloride with lead or copper nitrate solution. Benzyl alcohol, first formed by hydrolysis, is oxidised to benzaldehyde.

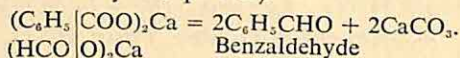


Benzyl chloride (10 g.), water (50 c.c.) and cupric nitrate (8 g.) are refluxed in a flask for about six hours, while a stream of carbon dioxide is passed through the system in order to prevent the oxidation of benzaldehyde by N_2O_5 or air. The liquid is cooled, and benzaldehyde extracted with ether. The extract is shaken with a saturated solution of sodium bisulphite, the crystalline bisulphite-compound separates. It is filtered, washed with ether, and finally decomposed with dilute H_2SO_4 . Benzaldehyde is again extracted with ether, dried, ether evaporated off on water-bath and the residue distilled.

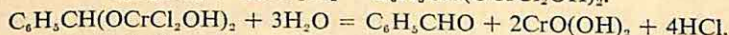
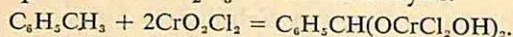
(2) Oxidation of benzyl alcohol with dilute nitric acid (p. 399), lead or copper nitrate gives benzaldehyde.



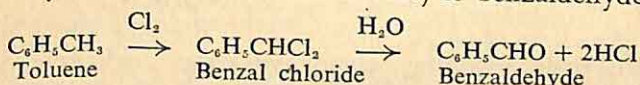
(3) Dry distillation of calcium benzoate and formate yields benzaldehyde (cf. aliphatic aldehydes, p. 132).



(4) Toluene, in carbon disulphide, is converted by chromyl chloride, CrO_2Cl_2 , to benzaldehyde at 25° - 45° ; oxidation does not proceed further. An explosive intermediate compound separates, which is removed and hydrolysed to benzaldehyde with cold water. This is *Etard's reaction* by which aromatic aldehydes are obtained from hydrocarbons. Industrially, toluene is oxidised by air, diluted with nitrogen, at 400° - 500° in presence of V_2O_5 to benzaldehyde.

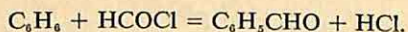


(5) Commercially, toluene is chlorinated to benzal chloride (p. 343) which is hydrolysed to benzaldehyde by heating with milk of lime under pressure, or with boiling water in presence of iron powder. It is purified by steam distillation. Boric acid hydrolyses benzal chloride (but not benzyl chloride or benzotrichloride) to benzaldehyde.

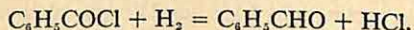


(6) Manganese dioxide and 65% H_2SO_4 oxidise toluene in liquid phase to benzaldehyde at about 40° in presence of copper sulphate. Some benzoic acid is also formed. The product, free from chlorine, is suitable for flavouring purposes. It is a commercial method.

(7) By passing carbon monoxide and dry HCl into benzene at about 50° in presence of anhydrous AlCl_3 and CuCl under 90 atmos. benzaldehyde is manufactured. Formyl chloride, HCOCl , believed to be formed, reacts with benzene. It is similar to Friedel-Crafts' reaction (p. 327) and may be applied to any aromatic hydrocarbon for directly introducing $-\text{CHO}$ into the nucleus. The reaction (*Gattermann* and *Koch*) proceeds more smoothly with alkylbenzenes.



(8) Hydrogen in presence of palladium reduces benzoyl chloride in xylene solution to benzaldehyde.



Properties.—Benzaldehyde is a highly refractive, colourless liquid (b.p. 179°), slightly soluble in water but highly soluble in alcohol and ether. It is volatile in steam and has the pleasant smell of bitter almonds. It is used as a flavouring agent and for making dyes such as malachite and brilliant greens, acridine orange R, benzoflavine, etc.

Reactions.—(i) Benzaldehyde is readily oxidised to benzoic acid on exposure to air. Crystals of benzoic acid are observed round the stopper

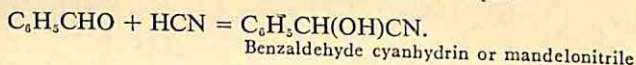
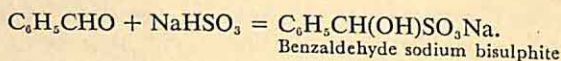
of the bottle containing benzaldehyde, which is opened frequently. During the *autoxidation* which is autocatalytic, perbenzoic acid, $C_6H_5CO-O-OH$, formed, oxidises another mol. of benzaldehyde (*cf.* peracetic acid, p. 127). Perfectly pure benzaldehyde does not suffer autoxidation. *Strong* HNO_3 does not oxidise benzaldehyde in the cold, but gives mainly *m*-nitrobenzaldehyde; *dilute* HNO_3 produces benzoic acid.



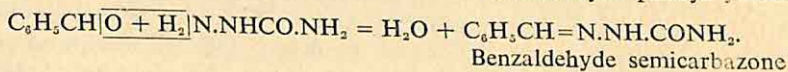
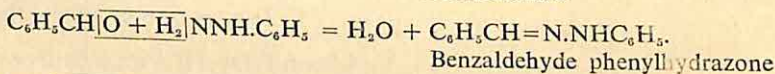
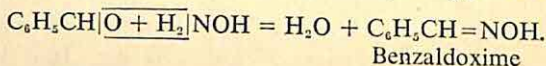
(ii) Benzaldehyde gives most of the reactions of aliphatic aldehydes. Thus, it is reduced by sodium amalgam to benzyl alcohol, $C_6H_5CH_2OH$, and converted into benzal chloride, $C_6H_5CHCl_2$, by PCl_5 (*cf.*, acetaldehyde, pp. 127-31).

(iii) Slowly it restores the colour of Schiff's reagent, and reduces ammoniacal silver nitrate but not Fehling's solution.

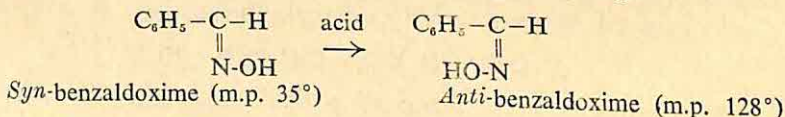
(iv) It forms a crystalline bisulphite-compound with $NaHSO_3$, and a cyanhydrin with HCN . The latter, on hydrolysis, gives mandelic acid, $C_6H_5CH(OH)COOH$.



(v) With hydroxylamine, phenylhydrazine, hydrazine, semicarbazide, etc., benzaldehyde reacts like acetaldehyde (pp. 128-29).



These derivatives exist in two stereoisomeric forms *syn* (or *cis*) and *anti* (or *trans*) like fumaric and maleic acid (p. 250), *e.g.*,



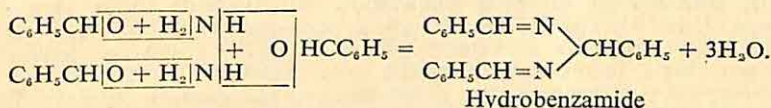
Unexpectedly, the *anti*-form of the oxime loses water more readily than the *syn*- when heated with acetic anhydride, and forms phenyl cyanide, C_6H_5CN .

Benzaldehyde differs from the aliphatic aldehydes as follows:

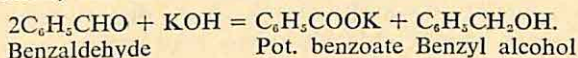
(i) Having no hydrogen in the α -position, benzaldehyde does not readily polymerise, even in presence of acids and alkalis, like acetaldehyde (p. 131). It behaves like $(CH_3)_3C.CHO$ in this respect (*cf.*, however (iv) on p. 403).

(ii) With ammonia it does not ordinarily form an aldehyde-ammonia, but gives a colourless, crystalline compound, hydrobenza-

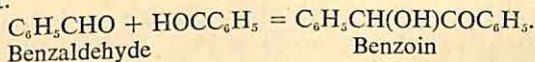
mide (m.p. 110°). Benzaldehyde-ammonia, $(C_6H_5CHO)_2NH_3$, is, however, formed at low temperature.



(iii) With concentrated aqueous caustic potash, it gives benzyl alcohol and benzoic acid by Cannizzaro reaction (p. 398), but *no resin*. This is characteristic of aldehydes having no hydrogen in the α -position (*vide*, p. 130). In the cold and with no excess of alkali, benzyl benzoate, $C_6H_5COO.CH_2C_6H_5$, is formed; this intermediate product is hydrolysed to the acid and the alcohol under usual conditions of Cannizzaro reaction. Hydroxy aromatic aldehydes, however, do not give this reaction, the mechanism of which is uncertain.

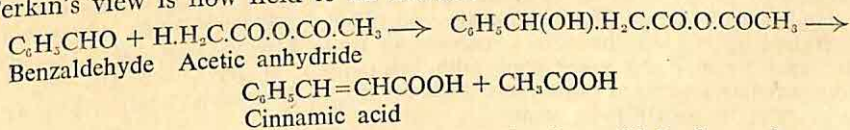


(iv) On refluxing with aqueous-alcoholic pot. cyanide, benzaldehyde forms benzoin, a ketonic alcohol. The reaction recalls aldol condensation (p. 131) and is known as *benzoin condensation*. Cyanide is a specific catalyst.

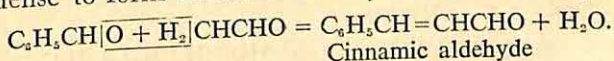


Benzoin, a colourless, crystalline solid (m.p. 137°), is both a ketone and a secondary alcohol. Like fructose, it contains the $-CHOH-CO-$ group, and so, reduces Fehling's solution. On oxidation with nitric acid, benzoin forms the diketone, *benzil*, $C_6H_5CO.CO.C_6H_5$, a yellow crystalline compound (m.p. 95°). On heating benzil with aqueous-alcoholic caustic potash for a while on a boiling water-bath, pot. benzilate is formed, from which *benzilic acid*, $(C_6H_5)_2C(OH)COOH$, in colourless needles (m.p. 150°) is obtained with dilute H_2SO_4 . This is *benzilic acid rearrangement*.

(v) Benzaldehyde, like other aromatic aldehydes, condenses on heating at 180° with the anhydride of a fatty acid in presence of its sodium salt (anhydrous) to give $\alpha\beta$ -unsaturated acids. Sodium carbonate or pyridine may replace sodium acetate which serves as a base (*Perkin's reaction*). According to Perkin (1877), the aldehyde condensed with the anhydride, and sodium acetate was the condensing agent; Fittig, however, thought that the anhydride was the condensing agent. Perkin's view is now held to be correct.



(vi) In presence of dilute caustic soda, benzaldehyde and acetaldehyde condense to form cinnamic aldehyde at room temperature.

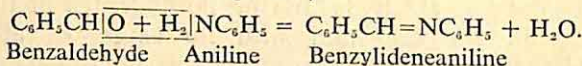


Cinnamic aldehyde, cinnamaldehyde, a liquid (b.p. 246°), is the main constituent of *oil of cinnamon* (obtained from the dried inner bark of cinnamon

trees which grow in Ceylon, South India, Java, etc.) and *oil of cassia*. It is widely used in perfumery and in flavouring essences.

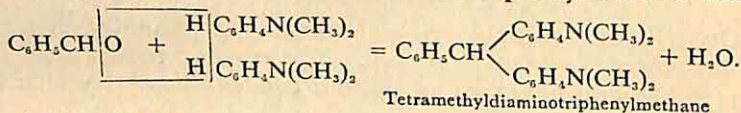
Similarly, with acetone at room temperature, benzaldehyde forms benzylidene acetone, $C_6H_5CH=CH.CO.CH_3$. Such a reaction between an aromatic aldehyde and other aldehydes or ketones with a $-CH_2-CO-$ group i.e., having two α -hydrogen atoms, in presence of caustic soda, is called *Claisen's reaction*. *Claisen's condensation* is, however, the condensation of an ester, in presence of sodium ethoxide, with another ester, a ketone or a nitrile (p. 197).

(vii) With aniline, benzaldehyde readily condenses, on warming, forming benzylideneaniline (m.p. 52°).

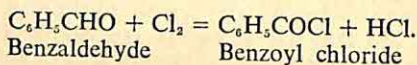


These condensation products of aldehydes and primary aromatic amines are called *anils* or *Schiff's bases*. On hydrolysis, they give the original aldehyde and amine; on reduction, secondary amines are formed.

(viii) With tertiary aromatic amines (e.g., dimethylaniline), benzaldehyde in presence of zinc chloride forms triphenylmethane derivatives.

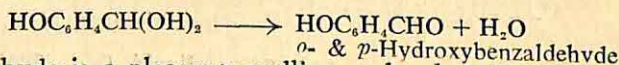
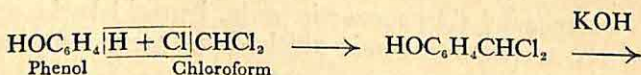


(ix) Benzaldehyde gives with dry chlorine at boiling temperature benzoyl chloride; there being no H at the α -carbon, the H of $-CHO$ is replaced by chlorine. In presence of a halogen carrier, *m*-chlorobenzaldehyde results.



Salicylaldehyde, *o*-hydroxybenzaldehyde, $C_6H_4(OH)CHO$, occurs in the oil of meadow-sweet. The glucoside, *salicin*, of willow bark (Latin *salix* willow) and poplar buds contains *saligenin*, *o*-hydroxybenzyl or salicyl alcohol, $C_6H_4(OH)CH_2OH$. Salicylaldehyde is obtained by oxidising saligenin with chromic acid. It may be made from phenol by *Reimer-Tiemann reaction*, discovered in 1876 in Hofmann's laboratory in Berlin in an attempt to see what happens when a primary amine is replaced by a phenol in the isocyanide reaction (p. 79).

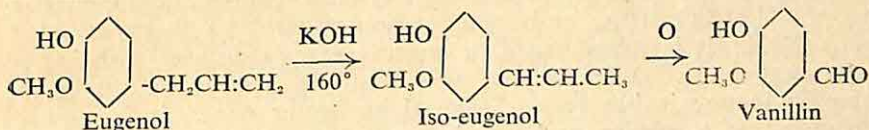
Phenol (1 part), chloroform (2 parts) and caustic potash (3 parts) are heated together to $60^\circ-70^\circ$ under reflux with water (5 parts) for nearly 2 hours. Salicylaldehyde with about 10% of its *p*-isomer is thus formed. The mixture is acidified with dilute H_2SO_4 and steam-distilled. Salicylaldehyde passes with steam leaving behind the solid *p*-compound (m.p. 116°). It is extracted with ether and purified by combining with bisulphite. It has a chelate ring of intramolecular hydrogen bond; the *p*-isomer forms hydrogen bond with water; this reduces its volatility in steam.



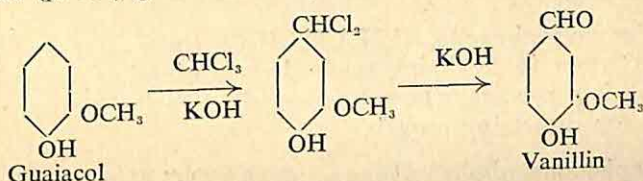
Salicylaldehyde is a pleasant-smelling, colourless liquid (b.p. 195°). In aqueous solution, it gives an intense violet coloration with ferric

chloride. On reduction, it forms saligenin, $C_6H_4(OH)CH_2OH$, and on oxidation, salicylic acid, $C_6H_4(OH)COOH$. Alkaline hydrogen peroxide oxidises it to catechol (p. 393). Salicylaldehyde does not reduce Fehling's solution or give Schiff's test, possibly due to chelate ring formation but reduces ammoniacal silver nitrate on prolonged standing. It stains the skin yellow.

Vanillin, *m*-methoxy-*p*-hydroxybenzaldehyde, $C_6H_3(OH)(OCH_3)CHO$, is the flavouring constituent of vanilla pods. On heating the pods, vanillin sublimes as colourless needles (m.p. 80°). Another source is eugenol, the chief constituent (80-90%) of oil of cloves and West Indian Bay oil (50%). The oil is heated with aqueous caustic potash; iso-eugenol thus formed, is oxidised to vanillin with nitrobenzene or ozone.



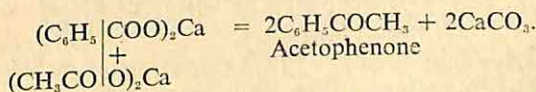
Guaiacol (p. 394) gives vanillin by Reimer-Tiemann reaction (p. 404).



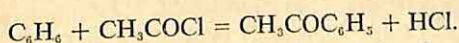
U.S.A. makes vanillin from lignin-sulphonate, a waste product in paper manufacture, by heating with alkali. Vanillin gives a blue colour with ferric chloride. It is a stronger acid ($k = 4.8 \times 10^{-6}$) than phenol.

The aromatic ketones or phenones, like the aliphatic, have the general formula $R.CO.R'$. They are of two types according as one or both the radicals, R and R', are aromatic; acetophenone, $C_6H_5.CO.CH_3$, and benzophenone, $C_6H_5.CO.C_6H_5$, are examples. These ketones exhibit the typical properties of the $-CO-$ group (p. 137) as well as aromatic character. They are solid with an agreeable odour. No aromatic ketone forms a bisulphite compound.

Acetophenone, phenylmethylketone, $C_6H_5.COCH_3$, occurs in coal-tar and some essential oils. Chromyl chloride oxidises ethylbenzene to acetophenone. It may be obtained (i) by the dry distillation of calcium benzoate and acetate. A little benzophenone and acetone are also formed.



(ii) More conveniently and in better yield, it is prepared by Friedel-Crafts' reaction (p. 327) from benzene and acetyl chloride or acetic anhydride:



Preparation.—Benzene (75 c.c.) and finely powdered, anhydrous aluminium chloride (30 g.) are taken in a dry flask fitted with a reflux condenser. The flask is cooled in cold water, and acetyl chloride (20 c.c.) is slowly added from a tap-funnel with shaking. The mixture is heated on water-bath at about 50° for an hour. When no more HCl evolves, it is cooled and poured into water.

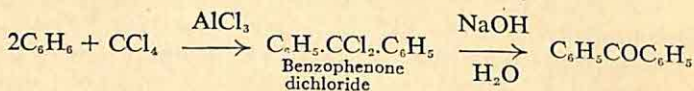
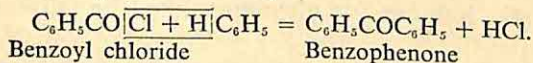
The upper oily layer contains acetophenone and benzene. It is washed with dilute caustic soda and dried with calcium chloride. Acetophenone is obtained by distillation.

(iii) Commercially, it is made by oxidising ethylbenzene, $C_6H_5CH_2CH_3$, with air in presence of vanadium pentoxide at 145° .

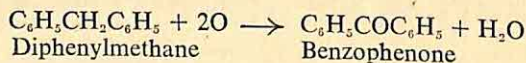
Properties.—Acetophenone is a colourless liquid (m.p. 20° , b.p. 202°) with a fragrant smell. It forms an oxime, a cyanhydrin, a hydrazone, etc. but little bisulphite compound due to the inhibiting action of the phenyl group. It is reduced to phenylmethyl carbinol, $C_6H_5CH(OH)CH_3$, by sodium and alcohol and to ethylbenzene by amalgamated zinc and HCl; selenium dioxide oxidises it to phenylglyoxal, $C_6H_5CO.CHO$, and pot. permanganate to benzoic acid, C_6H_5COOH . It is volatile with steam, and gives iodoform with iodine and caustic soda. Acetophenone was formerly a hypnotic under the name *hyponone*; it has been displaced by better ones. It is used in perfumery, as a solvent, and also in making styrene, certain dyes and pharmaceuticals.

ω -Chloroacetophenone, $C_6H_5.CO.CH_2Cl$ (m.p. 58°) (ω denotes the terminal C-atom in a chain), made by chlorinating acetophenone in acetic acid, is a relatively harmless but effective lachrymator (tear gas) employed for dispersing crowds.

Benzophenone, diphenylketone, $C_6H_5.CO.C_6H_5$, may be prepared by distilling calcium benzoate, or by the action of benzoyl chloride, carbon tetrachloride or carbonyl chloride on benzene in presence of aluminium chloride (Friedel-Crafts).



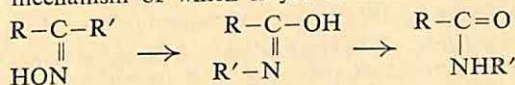
Diphenylmethane, on oxidation with chromic acid, forms benzophenone which resists further oxidation:



Properties.—The colourless, fragrant-smelling crystals of benzophenone are dimorphous. The ordinary, stable form (*rhombic*) melts at 49° ; this, on distillation, passes on to the unstable variety (*monoclinic*) melting at 26° . The latter changes to the stable form at all temperatures. It is insoluble in water but soluble in alcohol and ether. It yields an oxime but no bisulphite-compound or cyanhydrin. Sodium amalgam reduces it to benzhydrol or diphenyl carbinol, $C_6H_5CH(OH)C_6H_5$, a secondary alcohol; zinc and acetic acid give benzpinacol, $(C_6H_5)_2C(OH).C(OH)(C_6H_5)_2$ (cf., reduction of acetone p. 137). Heated in acetic acid with a little I_2 , it forms benzpinacolone,

$C_6H_5.CO.C(C_6H_5)_3$. On distilling with zinc dust, or reducing with hydriodic acid, diphenylmethane, $C_6H_5.CH_2.C_6H_5$, results. By fusion with caustic potash, we get benzene and pot. benzoate.

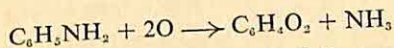
Ketoximes exist in syn- and anti-forms, their configuration may be determined as follows. In presence of H_2SO_4 , HCl or PCl_5 in ether, a ketoxime forms a substituted acid amide by intramolecular rearrangement known as *Beckmann transformation*. The transformation takes place only in the *anti*-position, the mechanism of which is yet obscure.



The amide, on hydrolysis, gives the corresponding primary amine, $R.NH_2$. By its identification, we know that R' was in the *anti*-position with respect to OH .

Quinones.—If two H atoms of the nucleus are replaced by two oxygen atoms, we get *quinones*. They are cyclic diketones, having no aliphatic analogue. Polycyclic compounds may have the keto groups in different rings. In quinones, the two keto groups are linked by conjugated double bonds. Only *o*- and *p*-quinones are known. Quinones have been isolated from flowering plants, fungi, bacteria, insects and lichens; their biological functions are not yet clear. *p*-Quinones are generally yellow solids with a pungent smell while *o*-quinones are usually orange or red. They sublime undecomposed and are volatile in steam with slight decomposition. They are readily reduced to dihydric phenols and so behave as oxidising agents. The simplest and most important is *p*-benzoquinone, simply called quinone.

Quinone, $C_6H_4O_2$, was first obtained in 1838 by oxidising quinic acid, $C_6H_7(OH)_4COOH$ (present in cinchona bark), whence the name. It may be prepared by suitably oxidising many *p*-substituted benzene derivatives such as quinol, *p*-phenylenediamine, *p*-amidophenol, *p*-phenolsulphonic acid, etc. Benzene can be directly oxidised to quinone with silver peroxide but the yield is poor. The usual method, however, is to oxidise aniline with pot. dichromate (or manganese dioxide) and sulphuric acid. The reaction is complex. Aniline black is an intermediate product.

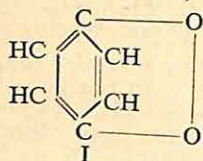


Aniline is dissolved in dilute H_2SO_4 and cooled; powdered pot. dichromate is slowly added with stirring. The temperature is kept below 50° . The product is extracted with ether. On evaporating the solvent, quinone crystallises. It is purified by sublimation.

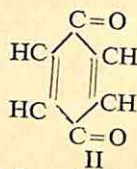
Quinone forms golden-yellow prisms (m.p. 116°) which turn brown on exposure to light. It has a pungent, pepper-like odour. It is slightly soluble in cold, but fairly soluble in hot, water and readily dissolves in alcohol and ether. Quinone is easily reduced by sulphur dioxide in water to quinol (p. 395) and forms quinihydrone (p. 395); on oxidation, it breaks up mainly into maleic acid (p. 250). It reduces ammon. silver nitrate in the cold, and liberates iodine from acidified pot. iodide solution. Quinone is volatile in steam. It is used in tanning.

Constitution of quinone.—(i) Quinol, *p*-dihydroxybenzene, $C_6H_4(OH)_2$, on mild oxidation, gives quinone, $C_6H_4O_2$, which can be reduced back to quinol. Many other *p*-substituted benzene derivatives yield quinone on oxidation. With

phosphorus pentachloride, quinone forms *p*-dichlorobenzene. So it is a *p*-compound. Quinone is, therefore, either



or



Benzenoid form (Graebe, 1867)

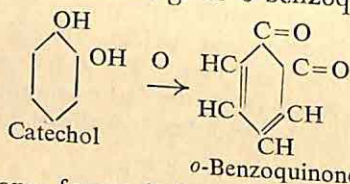
Quinonoid form (Fittig, 1863)

(ii) The peroxide structure (I) explains its oxidising action, but fails to account for (a) Quinone gives a mono- and a di-oxime with hydroxylamine, and so behaves as a diketone. (b) It combines, in chloroform solution, with bromine (and chlorine) at room temperature and in absence of sunlight and forms di- and tetra-bromide, $C_6H_4O_2Br_2$, and $C_6H_4O_2Br_4$. Quinone thus contains two and not three double bonds as required by (I). (c) Silver oxide breaks quinone mainly into maleic acid (p. 250). Quinone, therefore, has the quinonoid structure. (I) suggests the existence of *m*-quinones as yet unknown. Spatial and bond distance considerations also go against (I).

(iii) The parachor values for quinone agree with (II) which also accounts for its colour; this quinonoid grouping (a chromophore, p. 374) occurs in many coloured compounds.

Chloranil, tetrachloro-*p*-benzoquinone, $C_6Cl_4O_2$, is a fungicide, and an oxidant in the dye industry. It is obtained from aniline or phenol by heating with pot. chlorate and HCl (p. 387). Chlorination and oxidation take place simultaneously. It forms yellow plates (m.p. 290°), sparingly soluble in alcohol. Quinone, on chlorination, gives chloranil. Nitric acid oxidises pentachlorophenol, C_6Cl_5OH , to chloranil.

***o*-Benzoquinone**, $C_6H_4O_2$, is made by oxidising at room temperature catechol, in dry ether, with silver oxide in presence of anhydrous sodium sulphate which takes up the water formed. *o*-Aminophenol, $NH_2 \cdot C_6H_4 \cdot OH$, on oxidation, gives *o*-benzoquinone.



o-Benzoquinone forms light-red, crystalline plates which decompose at about 70° . It is reduced to catechol by sulphur dioxide in water. It is non-volatile and also odourless (*cf.* quinone). A second, colourless, prismatic form is also produced during the preparation, which readily passes on to the red variety. Both are identical chemically. The non-existence of *m*-quinones lends additional support to the constitution of *o*- and *p*-quinone. It is not possible to write down a similar structure for *m*-quinone. *o*-Benzoquinone is less stable than the para-isomer. It is a powerful oxidant, liberating iodine from acidified pot. iodide.

QUESTIONS

- How do you prepare (a) salicylaldehyde, (b) cinnamic aldehyde, (c) vanillin and (d) acetophenone?
- What is the action of HNO_3 on (a) alcohol, (b) benzaldehyde, (c) glycerol, and (d) toluene? State the conditions of the reactions necessary in each case.

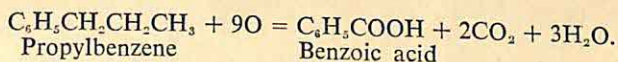
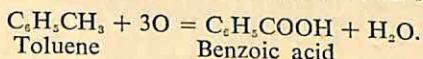
3. How is benzaldehyde prepared? Compare and contrast its properties with those of acetaldehyde. B.Sc. Pass, 1935, Dacca Uni. and B.A. & B.Sc. Degree Exam. 1934, Andhra Uni.
4. Compare and contrast the properties of aliphatic and aromatic aldehydes. B.A. and B.Sc. 1937, Bombay Uni; Punjab Uni B.Sc. Hons. 1922.
5. How is benzaldehyde obtained from toluene? What is the reaction of benzaldehyde with (a) KOH, (b) HCN, (c) KCN, and (d) chlorine? B.A., Pass, 1938, Bombay Uni.
6. How would you differentiate between any of the following: (i) ethyl nitrate and nitro-ethane, (ii) phenol and benzyl alcohol, (iii) ethyl propionate and propyl acetate, (iv) acetaldehyde and benzaldehyde? B.A. and B.Sc. Pass, 1935, Allahabad Uni.
7. Give some account of the preparation and properties of the benzo-quinones. B.Sc. London, 1925.
8. How would you prepare benzaldehyde starting from (a) benzene, (b) toluene, and (c) benzoic acid? Explain the reactions involved in each case. B.Sc. Pass, 1936, Calcutta Uni.
9. The contents of four unlabelled bottles are known to be (a) cyclo-hexanol, (b) ethylene glycol, (c) acetophenone and (d) phenetole. Describe experiments you would perform in order that the bottles could be accurately labelled. A.I.C. 1941.
10. How would you prepare from benzaldehyde: benzoic acid, benzyl alcohol, benzylidene chloride, benzoin, benzil, mandelic acid and cinnamic acid?
11. Write short notes on the following: (a) the Friedel-Crafts' reaction, (b) the benzoin condensation, (c) the Cannizzaro reaction, (d) aldol condensation, and (e) the Reimer-Tiemann reaction. B.Sc. Degree Exam., 1941, Anna-malai Uni.
12. How is benzaldehyde prepared on a large scale? Compare its properties with those of aliphatic aldehydes. What is the action of KCN, ammonia, and NaOH on it? B.Sc. 1942, Agra Uni.
13. Write an essay on the uses of Friedel-Crafts' Reaction in Organic Chemistry. B.A. & B.Sc., 1936, Andhra Uni.
14. How would you prepare benzaldehyde from toluene? State its reactions and show in what respects they differ from those of acetaldehyde. Give equations. B.Sc. 1950, Gauhati Uni.,; B.A. Degree Exam. 1941, Madras Uni.
15. 0.836 g. of a compound, treated with HI, gave CH_3I which, with excess of alcoholic AgNO_3 , produced 1.424 g. AgI . On oxidation, it passed on to $\text{C}_6\text{H}_5\text{O}_3$. If the molecular formula of the compound is $\text{C}_8\text{H}_{10}\text{O}_2$, what is its possible structure? Ans. $\text{C}_6\text{H}_4(\text{OCH}_3)\text{CH}_2\text{OH}$, *o*-, *m*- or *p*-.

CHAPTER XLI

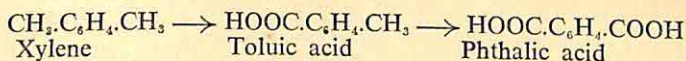
THE AROMATIC CARBOXYLIC ACIDS

The aromatic carboxylic acids are derived from the aromatic hydrocarbons by the replacement of one or more H-atoms by a corresponding number of -COOH groups. The carboxyl may be linked to the nucleus or to the side-chain; this, makes no appreciable difference in their behaviour. Benzoic acid, C_6H_5COOH , phthalic acids, $C_6H_4(COOH)_2$, etc., are true aromatic acids and belong to the first group, while phenylacetic acid, $C_6H_5CH_2COOH$, cinnamic acid, $C_6H_5CH=CHCOOH$, etc., are aryl-substituted aliphatic acids and come under the second. The aromatic acids resemble the aliphatic in forming salts, esters, anhydrides, etc. But due to the presence of the negative phenyl group, they are somewhat stronger acids (k for n -caproic acid is 1.4×10^{-5} , but for benzoic acid, 6.86×10^{-5}). Any substituent (but not m - or p -) of benzoic acid, gives a stronger acid. They are less soluble in water owing to higher proportion of C to COOH; the aromatic acids are much less volatile and melt at a much higher temperature than aliphatic acids of similar mol. wt. The carboxyl in an aromatic acid is more readily reduced than in an aliphatic acid; benzoic acid gives benzaldehyde on electrolytic reduction, and benzyl alcohol with sodium amalgam. They are readily halogenated, nitrated or sulphated. On heating with soda-lime (and sometimes alone), these acids split off carbon dioxide; benzoic acid, C_6H_5COOH , thus gives benzene; gallic acid, $C_6H_2(OH)_3COOH$, forms pyrogallol, $C_6H_3(OH)_3$ (cf., formation of methane from sodium acetate, p. 41).

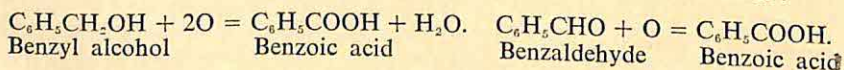
General methods of preparation.—(1) Aromatic acids are commonly obtained by oxidising homologues of benzene with dilute nitric acid, chromic acid, or alkaline pot. permanganate. A side-chain is thus converted into a -COOH group; the longer the chain, the easier the oxidation. Evidently, we thus obtain only acids with -COOH attached to the nucleus. By passing toluene vapour and air over vanadium pentoxide at about 400° , benzoic acid is manufactured.



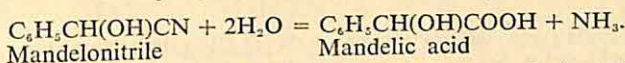
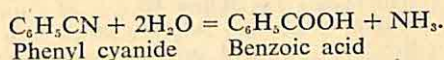
If there be more than one side-chain, oxidation may be limited to one or all the side-chains; dilute nitric acid generally oxidises one while chromic acid in acetic acid, or alkaline pot. permanganate all the side-chains, to -COOH. The longer of two side-chains is oxidised first.



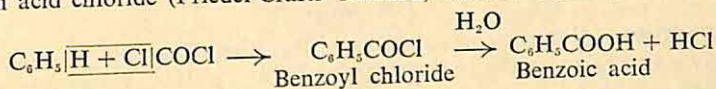
(2) Oxidation of aromatic alcohols or aldehydes gives aromatic acids:



(3) Hydrolysis of aryl cyanides (or nitriles) results in aromatic acids. The nitriles may be obtained from diazo-salts by Sandmeyer's reaction (p. 367), or by distilling potassium sulphonates with pot. cyanide (p. 380).

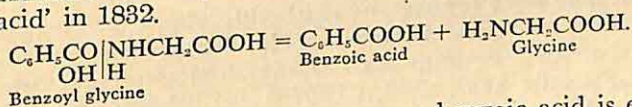


(4) Carbonyl chloride and a hydrocarbon in presence of aluminium chloride form an acid chloride (Friedel-Crafts' reaction) which is hydrolysed to acid :



Carbonyl chloride must be in excess otherwise ketones are formed (cf. preparation of benzophenone, p. 406). Benzene and carbon dioxide (at about 60 atmospheres) react at 100° in presence of aluminium chloride to form benzoic acid and benzophenone, $\text{C}_6\text{H}_5\text{CO} \cdot \text{C}_6\text{H}_5$.

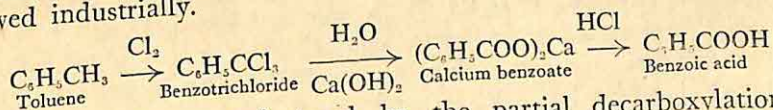
Benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$, one of the earliest known organic acids, occurs free in cranberries, gum benzoin, etc. and as the benzyl ester, $\text{C}_6\text{H}_5\text{CO} \cdot \text{O} \cdot \text{CH}_2\text{C}_6\text{H}_5$ in many resins such as gum benzoin, Peru balsams, etc. On heating the resin, the acid sublimes off. As benzoyl-glycine or hippuric acid (*hippos* horse), it is present in the urine of herbivorous animals, notably (about 2%) in the urine of horses and cattle. It may be obtained therefrom by hydrolysing with moderately strong hydrochloric acid; Scheele thus obtained it in 1785. Liebig and Wöhler established its composition in their classical paper 'The radical of benzoic acid' in 1832.



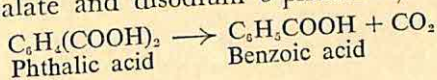
Preparation.—(1) For medicinal use, some benzoic acid is even now obtained from gum benzoin by sublimation.

(2) The general methods are applicable for its preparation. Benzaldehyde gives benzoic acid by Cannizzaro reaction (p. 403).

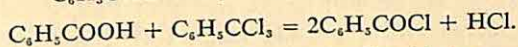
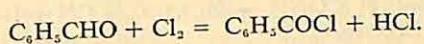
(3) Commercially, toluene is chlorinated to benzotrichloride, $\text{C}_6\text{H}_5\text{CCl}_3$ (p. 343) which is hydrolysed at 50° with milk of lime in presence of iron powder to calcium benzoate. Benzoic acid is liberated with dilute mineral acid. This, being sparingly soluble in cold water, separates and is purified by recrystallisation from hot water. Oxidation of toluene by air in presence of stannic vanadate to benzoic acid is also followed industrially.



(4) It is also manufactured by the partial decarboxylation of phthalic acid (obtained from naphthalene) by heating with lime, or heating phthalic anhydride with steam at 200° in presence of catalyst (chromium o-phthalate and disodium o-phthalate).

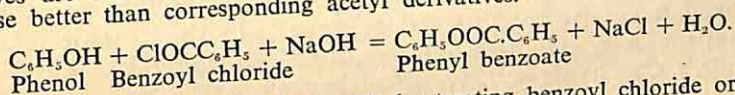


by passing chlorine into boiling benzaldehyde until no more hydrochloric acid is evolved (p. 404), or heating benzoic acid with benzotrichloride.



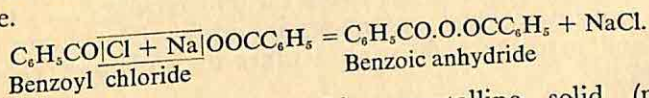
Benzoyl chloride is a colourless, oily liquid (sp. gr. 1.21) with a pungent and irritating smell. Its vapour causes watering of the eyes. It is very slowly hydrolysed by hot water or dilute caustic soda (*cf.*, aliphatic acid chlorides). It readily forms crystalline derivatives with compounds containing $-\text{OH}$, $-\text{NH}_2$ or $-\text{NH}-$ groups by replacing the hydrogen with benzoyl group, $\text{C}_6\text{H}_5\text{CO}-$. The process, called *benzoylation* (*cf.*, acetylation, p. 162), helps detection of these groups in organic compounds.

Benzoylation is done by vigorously shaking the solution or suspension of the compound in excess of 10% aqueous caustic soda with a small excess of benzoyl chloride (*Schotten-Baumann reaction*). The insoluble benzoyl derivative crystallises. Caustic soda and the excess of benzoyl chloride form sodium benzoate which remains in solution. Pyridine may be added in place of caustic soda to absorb the hydrochloric acid formed. *p*-Nitrobenzoyl chloride, $\text{NO}_2\text{C}_6\text{H}_4\text{COCl}$, may be tried if the benzoyl derivative does not crystallise well. Benzoylation is sometimes preferred to acetylation in identifying organic compounds as this can be carried out in presence of water; furthermore, benzoyl derivatives are less soluble in most solvents, have higher m.p. and generally crystallise better than corresponding acetyl derivatives.



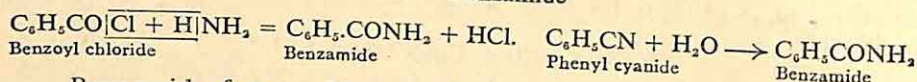
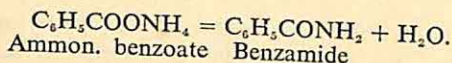
Benzoyl peroxide, $(\text{C}_6\text{H}_5\text{CO})_2\text{O}_2$, made by treating benzoyl chloride or benzoic anhydride with ice-cold aqueous sodium peroxide, is a white solid (m.p. 104°). It is fairly stable, and employed for bleaching and as a catalyst in some polymerisation reactions. Benzoyl peroxide and sodium ethoxide in alcohol form sodium perbenzoate which with acids gives *perbenzoic acid*, $\text{C}_6\text{H}_5\text{CO}\cdot\text{O}\cdot\text{OH}$, (m.p. 41°). The acid converts a non-conjugated double bond into an ethylene oxide derivative quantitatively and is useful for estimating such double bonds. It liberates iodine from pot. iodide quantitatively.

Benzoic anhydride, $(\text{C}_6\text{H}_5\text{CO})_2\text{O}$, is prepared by heating benzoyl chloride and dry sodium benzoate (*cf.*, preparation of acetic anhydride, p. 163), or slowly distilling benzoic acid with an excess of acetic anhydride.

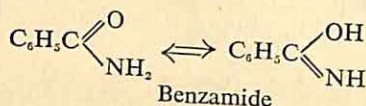


Benzoic anhydride is a white crystalline solid (m.p. 42°), resembling acetic anhydride but much less reactive. It is practically unaffected by cold water; boiling water slowly decomposes it to benzoic acid. It benzoylates alcohols, phenols and amines.

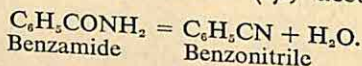
Benzamide, $\text{C}_6\text{H}_5\text{CONH}_2$, is obtained by heating ammonium benzoate in a sealed tube (*cf.*, preparation of acetamide, p. 165), or better, by the action of aqueous ammonia or ammonium carbonate on benzoyl chloride at ordinary temperature. Ethyl benzoate and ammonia also form benzamide. Partial hydrolysis of phenyl cyanide with alkaline hydrogen peroxide gives benzamide.



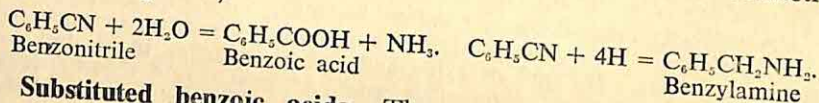
Benzamide forms white crystals (m.p. 130°), soluble in hot water. Like acetamide, it is hydrolysed to benzoic acid by acids, and more rapidly by alkalis. It gives metallic derivatives such as mercury benzamide, $(\text{C}_6\text{H}_5\text{CONH})_2\text{Hg}$, with mercuric oxide, and both N- and O-ethers. This is explained by assuming that benzamide exists in tautomeric forms; the H of the -OH is replaceable by metals like Na, Ag, etc.



Benzonitrile, phenyl cyanide, $\text{C}_6\text{H}_5\text{CN}$, is prepared by heating benzamide with phosphorus pentoxide (*cf.*, acetonitrile).



It can also be made by Sandmeyer's reaction from diazo-salts with pot. cyanide (p. 368), or by fusing pot. benzenesulphonate with pot. cyanide, but *not* by reacting iodobenzene with the cyanide (*cf.* p. 74). Benzonitrile is a colourless oil (b.p. 190°), smelling like oil of bitter almonds. On hydrolysis, it gives benzoic acid, and on reduction, benzylamine (p. 362).

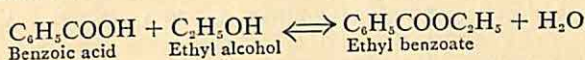


Substituted benzoic acids.—The carboxyl group deactivates the benzene ring and is meta-directing; substitution in the ring is rather difficult. Meta-substituted benzoic acids may be directly obtained by nitration, halogenation, sulphonation, etc. The *o*- and *p*-derivatives are prepared by the oxidation of the corresponding toluenes; *e.g.*, *o*- and *p*-chlorotoluenes yield, on oxidation, *o*- and *p*-chlorobenzoic acids. Chlorination of benzoic acid furnishes the *m*-compound. Nitrobenzoic acids, on reduction, give aminobenzoic acids. The latter may be diazotised and made to yield various other derivatives of benzoic acid (*cf.*, pp. 367-68).

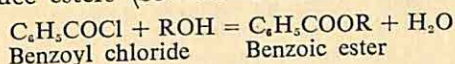
Anthranilic acid, *o*-aminobenzoic acid, $\text{C}_6\text{H}_4(\text{NH}_2)\text{COOH}$, was first obtained from indigo by alkali fusion and then employed for making indigo. It may be made by reducing *o*-nitrobenzoic acid or heating *o*-nitrotoluene with alcoholic caustic soda (internal oxidation); it is manufactured from phthalimide (obtained from naphthalene) and alkaline hypochlorite. The acid, an important dye intermediate, is a white solid (m.p. 145°), sparingly soluble in water and alcohol. The aqueous solution tastes sweet. On heating to 205° , it decomposes into aniline and carbon dioxide. Its sweet-smelling methyl ester occurs in orange blossom and jasmine flowers. *p*-Aminobenzoic acid (m.p. 174°)

is vitamin Bx; its ethyl ester, *benzocaine*, is a local anæsthetic; *novocaine*, $\text{H}_2\text{NC}_6\text{H}_4\text{COOCH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$, is another.

Esters of benzoic acid are prepared by refluxing a mixture of benzoic acid, absolute alcohol and about 3% by wt. of dry hydrochloric acid gas for nearly three hours (*Fischer-Speier method*). The excess of alcohol is distilled off, and the free acid removed with sodium carbonate solution. The oily ester is separated, washed with water, dried with fused calcium chloride and distilled (*cf.*, ethyl acetate, p. 169).

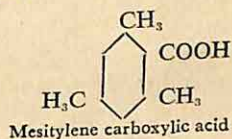
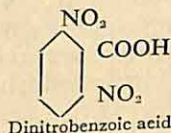
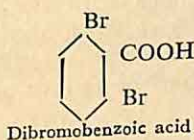


In presence of caustic soda, alcohols or phenols act upon benzoyl chloride to produce esters (*Schotten-Baumann reaction*, p. 413).

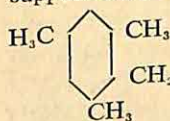


Ethyl benzoate is a colourless, heavy liquid (b.p. 213°) with a smell of peppermint. *Methyl benzoate* (b.p. 199°), isomeric with phenyl acetate, $\text{CH}_3\text{COOC}_6\text{H}_5$, is a perfume. *Phenyl benzoate*, $\text{C}_6\text{H}_5\text{COOC}_6\text{H}_5$ (derived from phenol and benzoyl chloride) is a crystalline solid (m.p. 71°). These esters are hydrolysed by boiling alkalis less readily than the aliphatic. On catalytic reduction at about 150° , ethyl benzoate gives benzyl alcohol; with sodium and alcohol, it forms toluene.

Esters of substituted benzoic acids.—Monosubstituted benzoic acids are readily esterified but di-ortho-substituted benzoic acids form little or no ester by Fischer-Speier method. This is independent of the nature of the substituent groups. The following acids produce no ester with alcohols:



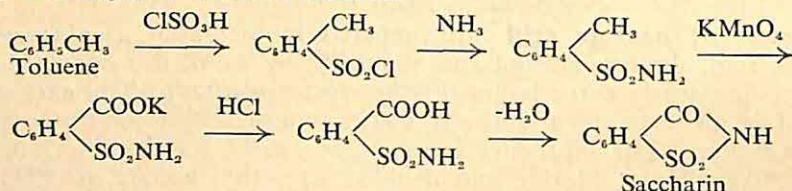
According to Victor Meyer (1848-97), the substituents in close proximity to the $-\text{COOH}$ exert a protective influence on the latter, so that alcohol molecules are prevented from coming in contact with it. Consequently, there is no reaction. This is known as *steric hindrance* or *spatial interference*. It is supported by the fact that mesitylacetic acid,



(but not mesitylene carboxylic acid) in which the carboxyl group is at the end of a chain, (but not mesitylene carboxylic acid) can be esterified as it is outside the sphere of protection. Esters of di-ortho-substituted acids can, however, be prepared from alkyl iodides and their silver salts. Once formed, it is again difficult to hydrolyse these esters.

Saccharin, *o*-sulphobenzoimide, was accidentally discovered by the American chemist, Ira Remsen and his pupil, Fahlberg in 1879. After laboratory work, they were taking tea which tasted extraordinarily sweet. The cause was traced to this compound sticking to their fingers. Saccharin is commercially made from toluene which, on sulphonation with chlorosulphonic acid, forms *o*- and *p*-toluenesulphonic chlorides. The oily *o*-derivative (separated from its solid *p*-isomer by freezing) is converted into toluene-*o*-sulphonamide, $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2$, by treating with ammonia or ammonium carbonate. This is oxidised with alkaline pot. permanganate to the alkali salt of *o*-sulphon-

amide of benzoic acid, $\text{KO}_2\text{CC}_6\text{H}_4\text{SO}_2\text{NH}_2$. On acidification, it loses water to form the anhydride which is saccharin.



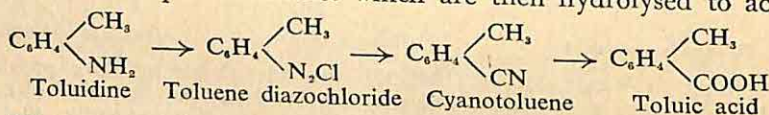
Saccharin is a white, crystalline solid (m.p. 220°), slightly soluble in water. The hydrogen of the $-\text{NH}-$ group is acidic and replaceable by metals. It is nearly 550 times sweeter than cane-sugar, and is largely used as a sweetening material in tooth pastes, beverages and foodstuffs. It has no food value. The sodium or ammonium salt, which is soluble in water, is generally used in concentration of about 1:10,000. A strong solution tastes *bitter*. In small doses, saccharin is harmless, but in large quantities, it has an anti-fermentation action. Diabetics take saccharin instead of cane-sugar which they cannot assimilate.

The ammonium salt, *sucramine*, is still sweeter. The anion, $\text{C}_6\text{H}_4 \begin{array}{l} \text{CO} \\ \text{SO}_2 \end{array} \text{N}^-$,

in solution from saccharin or its salts, is responsible for sweetness which increases with dilution. When the imide H is replaced by ethyl group, we get a tasteless compound.

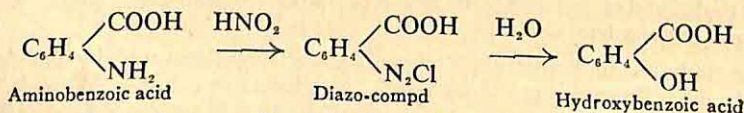
p-Toluenesulphonic chloride, a bye-product, is converted with ammonia into the sulphochloramide, called *chloramine T* or *activin*. It is a valuable antiseptic and scouring agent for cotton.

Toluic acids, methylbenzoic acids, $\text{C}_6\text{H}_4(\text{CH}_3)\text{COOH}$, are produced by partial oxidation of *o*-, *m*- and *p*-xylenes with hot, dilute nitric acid (p. 333). They may as well be prepared from the corresponding toluidines by converting them, by diazo- and Sandmeyer's reaction, into respective nitriles which are then hydrolysed to acids:

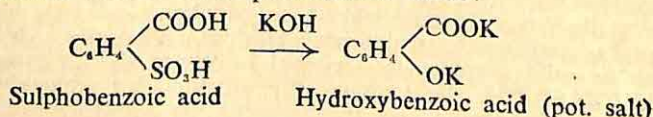


These are isomeric with phenylacetic acid, $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$, (m.p. 76°) which, on oxidation, gives benzoic acid; but toluic acids form phthalic acids. The *o*-, *m*- and *p*-toluic acids melt respectively at 103° , 110° and 180° . They closely resemble benzoic acid in their properties. *o*-Toluic acid is much stronger than the *m*- or *p*-.

The phenolic acids contain both phenolic $-\text{OH}$ and $-\text{COOH}$ groups. These may be prepared (1) from aromatic amino-acids by diazo-reaction, and boiling the diazo-salt in water:



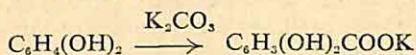
(2) By alkali fusion of sulphobenzoic acids:



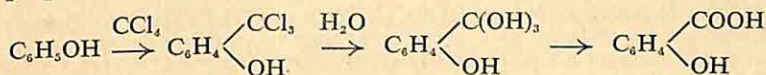
(3) By passing carbon dioxide over dry sodium phenate at about 150° (*Kolbe's method*):



(4) By heating di- or tri-hydric phenols with aqueous ammonium or potassium carbonate to $100\text{--}130^{\circ}$.



(5) On boiling phenol, caustic soda and carbon tetrachloride together, *o*- and *p*-hydroxybenzoic acids (as disodium salts) are formed (*cf.*, preparation of salicylaldehyde, p. 404):



Properties.—Phenolic acids are colourless, crystalline solids, more soluble in water and less volatile than their parent acids. Chemically, they behave both as phenols and as carboxylic acids. Many have antiseptic properties. The *o*-compounds produce, unlike their *m*- and *p*-isomers, a violet or blue coloration with neutral ferric chloride, and are also volatile in steam. The acids form esters as well as ethers. Heated alone or with soda-lime, they lose carbon dioxide and form phenols.

Salicylic acid, *o*-hydroxybenzoic acid, $\text{C}_6\text{H}_4(\text{OH})\text{COOH}$, occurs in some essential oils, and was first obtained by Piria (1838) from *salicin* (p. 404), hence the name. Its methyl ester is the main constituent of *oil of wintergreen*. The acid may be prepared by methods on pp. 416-17; it is manufactured by modified Kolbe's method:

Dry sodium phenate is heated to 130° in an autoclave with carbon dioxide under about 100 lb. pressure for several hours. Sodium phenyl carbonate formed gives, by molecular rearrangement, sodium salicylate almost quantitatively. The mass is extracted with water and salicylic acid liberated with a mineral acid. It is recrystallised from hot water or sublimed. With potassium phenate, the main product is *p*-hydroxybenzoic acid at 150° and above. Pharmaceutical salicylic acid is prepared by saponifying oil of wintergreen with potash.

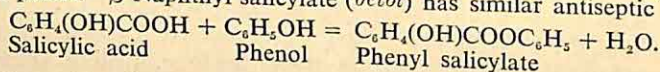


Properties.—Colourless, fluffy needles of salicylic acid (m.p. 159°) are sparingly soluble in cold water but readily dissolve in hot water, alcohol, and ether. It is much stronger than the *m*- or *p*-isomer due to bridge formation by phenolic H with carbonyl O, which causes electron displacement towards the H-bond. The acid produces, like phenol and resorcinol, an intense violet coloration with ferric chloride. On *rapidly* heating, it sublimates with slight decomposition. But on *slow* distillation, or when heated with lime, it decomposes mainly into phenol and carbon dioxide. It forms a mono-sodium salt, $\text{C}_6\text{H}_4(\text{OH})\text{COONa}$, with sodium carbonate and a disodium salt, $\text{C}_6\text{H}_4(\text{ONa})\text{COONa}$, with caustic soda. Bromine-water forms 2:4:6-tri-bromophenol bromide, $\text{C}_6\text{H}_2\text{Br}_3\text{OBr}$, quantitatively—a reaction by which it is estimated. Bromine replaces the —COOH in aqueous medium

giving 2:4:6-tribromophenol, but in nitrobenzene solution, *o*-hydroxy-*p*-bromobenzoic acid results. With fuming nitric acid, 2:4:6-trinitrophenol is obtained from salicylic acid.

Uses.—Salicylic acid is an odourless antiseptic and antipyretic. Its solution in collodion removes corns. It is a food preservative, and also used in making some azo-dyes and perfumes. Phenyl salicylate (*salol*) and acetyl salicylic acid (*aspirin*) are common drugs. Salol passes through the acidic stomach unchanged but in the alkaline intestine, it is slowly hydrolysed to phenol and salicylic acid which act as antiseptic separately. Sodium salicylate is a remedy for rheumatism. Salicylanilide (*Shirlan*) is a preservative for cotton size.

Methyl salicylate, $C_6H_4(OH)COOCH_3$, (b.p. 224°) is used in rheumatism, sprains and bruises and also as a perfume. It may be obtained from salicylic acid by heating with methyl alcohol and H_2SO_4 . *Phenyl salicylate* $C_6H_4(OH)COOC_6H_5$, is prepared by heating salicylic acid and phenol with carbonyl chloride or phosphorus oxychloride; it is a white, crystalline solid (m.p. 43°), used in some tooth pastes. β -Naphthyl salicylate (*bctol*) has similar antiseptic properties.



Aspirin, acetyl salicylic acid, $C_6H_4(OCOCH_3)COOH$, is obtained by acetylating the acid with acetyl chloride or acetic anhydride in a suitable solvent, e.g., benzene. It is a white solid (m.p. 135°), sparingly soluble in water. Aspirin relieves headache and neuralgic pain. About 13 million lb. are consumed annually in U.S.A. *p*-Aminosalicylic acid, 2-hydroxy-4-aminobenzoic acid (PAS), is given with streptomycin to combat tuberculosis. In 1957 India imported 1,42,763 kg. of it, valued at Rs. 24,27,896.

Anisic acid, *p*-methoxybenzoic acid, $CH_3OC_6H_4COOH$, (m.p. 184°) is isomeric with methyl salicylate. It is obtained by oxidising anethole (p. 388) with chromic acid. It gives anesole (p. 388) on heating with soda-lime.

Protocatechuic acid, 3:4-dihydroxybenzoic acid, $C_6H_3(OH)_2COOH$, is the most important of the six dihydroxybenzoic acids, and is derived from catechol by heating with ammonium carbonate and water at 140° . It results when certain resins, alkaloids, tannins, anthocyanins, etc. are fused with potash. Protocatechuic acid forms colourless, monohydric crystals which gradually turn black on exposure to light. At 100° , the anhydrous acid (m.p. 199°) is obtained. It behaves like catechol and benzoic acid. On heating, it loses carbon dioxide and yields catechol. It reduces ammoniacal silver nitrate (cf., catechol, p. 394) and gives a green colour with ferric chloride. It is highly soluble in water.

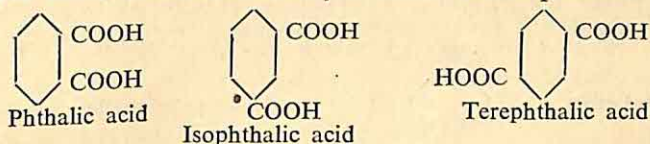
Gallic acid, 3:4:5-trihydroxybenzoic acid, $C_6H_2(OH)_3COOH$, occurs as a glucoside, and also in the free state in various plant products such as tannins of gall nuts, tea, etc. It is best obtained by boiling gall nut extract with dilute acids and extracting the gallic acid with ether, in which tannin is insoluble. The acid crystallises in monohydric needles (m.p. 222°) and becomes anhydrous at 120° . It is readily soluble in alcohol, ether and boiling water. It reduces Fehling's solution and absorbs oxygen in alkaline solution like pyrogallol (p. 396). On heating, gallic acid loses carbon dioxide and forms pyrogallol, $C_6H_3(OH)_3$. Its aqueous solution produces with ferric salts a blue-black precipitate, and so used as a marking ink. Pyrogallol, some inks, drugs and a few dyes are made from it.

Tannins or tannic acid is the name given to certain astringent, amorphous and practically colourless substances occurring in the bark, wood, leaves, etc. of plants. The tannin content of woods varies widely with the species. Tannins are of two types: polyesters or depsides which are hydrolysable, and the catechol tannins or phlobatannins which are condensation products and not hydrolysable. Tannins are mostly soluble in boiling water and alcohol but

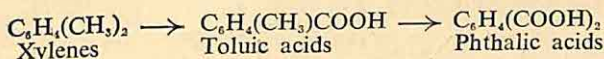
almost insoluble in ether; hot mineral acids decompose them. They form insoluble compounds with gelatine and other proteins, certain alkaloids, and metallic salts. They are consequently used in protecting hides from putrefaction; the process is called *tanning*. Tanned hide is leather. Tannins are also employed in dyeing as a mordant; they form insoluble, coloured stuffs with basic dyes. They are used as an astringent, for treating burns and diarrhoea and in making ink. Indian *Myrabolan* and *Acacia catechu* are important commercial sources for tannic acid. Chinese tannin is a penta-ester of gallic acid with glucose. In U.S.A., tannic acid is extracted from nutgalls with water saturated with ether. It is a light yellow powder.

Ink.—Gallic acid forms a pale brown solution with ferrous salts, which, on atmospheric oxidation, turns blue-black. Ordinary writing inks are mixtures of gallic acid, ferrous sulphate, a little dilute H_2SO_4 (which retards rapid oxidation) and gum arabic as a protective colloid. Indigo carmine or alizarin blue is added to deepen the colour, and a phenol as preservative. Such a mixture writes blue, the acid is neutralised by the alumina in the paper and oxidation changes it to deep blue which is the ferric salt.

The phthalic acids.—The most important of the aromatic dibasic acids are the three benzenedicarboxylic acids, called phthalic acids:

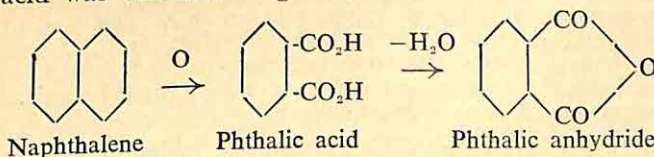


These may be prepared by the oxidation of the corresponding xylenes with dilute nitric acid, or toluic acids with alkaline pot. permanganate.



These form both acid and normal salts and esters. The *o*-compound yields an inner anhydride but not the other two due to the distance of $-COOH$ groups. Phthalic acid ($k_1 = 1.26 \times 10^{-3}$) is stronger than isophthalic acid ($k_1 = 2.9 \times 10^{-4}$) or terephthalic acid ($k_1 = 1.5 \times 10^{-4}$). On heating with soda-lime, they first give benzoic acid and finally, benzene: $C_6H_4(COOH)_2 \rightarrow C_6H_5COOH \rightarrow C_6H_6$.

Phthalic acid, benzene-*o*-dicarboxylic acid, $C_6H_4(COOH)_2$, was formerly made by oxidising naphthalene, $C_{10}H_8$, with fuming sulphuric acid at about 300° in presence of a little mercury or mercuric sulphate as catalyst, discovered by accident in 1897. The mercury thermometer broke while stirring with it during sulphonation of naphthalene, phthalic acid was obtained in good yield.



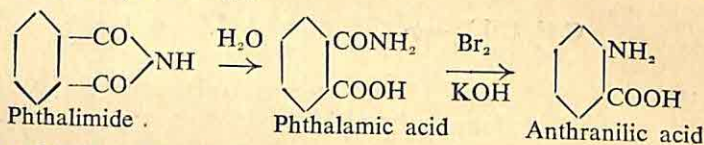
The oxidation is now carried out by passing naphthalene vapour with excess air over vanadium pentoxide at about 360° . The yield is almost quantitative; a little maleic acid is formed as a bye-product. Phthalic acid distils as the anhydride which, on boiling with water,

yields the free acid. *o*-Xylene is similarly oxidised to phthalic acid commercially. Phthalic acid forms colourless plates (m.p. 231° with the formation of anhydride). It is moderately soluble in water, alcohol, and ether but insoluble in chloroform.

Phthalic anhydride is largely used for making fluorescein, indigo, eosin and some other dyes. Cheap phthalic acid from naphthalene made the commercial synthesis of indigo a success. Anthraquinone (q.v.) is manufactured from phthalic anhydride. Dimethyl phthalate is a plasticiser, and an effective mosquito repellent; diethyl phthalate is a solvent for cellulose acetate lacquer. Phthalic acid and its metallic salts prevent the growth of mildew in paints in damp, warm climate. Synthetic plastics such as *Glyptals* are made from phthalic anhydride and glycerine.

Phthalic anhydride, $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{smallmatrix} \text{O}$, may be obtained by heating phthalic acid to about 200° ; it is manufactured by catalytic oxidation of naphthalene or *o*-xylene by air and purified by sublimation. It forms white needles (m.p. 128°). Phthalic anhydride is used in making dyes, alkyl resins with polyhydric alcohols (used in protective coatings), plasticizers and insect repellents.

Phthalimide, $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{smallmatrix} \text{NH}$, is made from phthalic anhydride and dry ammonia under pressure at 300° . Ammon. phthalate or phthalamide gives phthalimide on heating. It forms a potassium salt with alcoholic caustic potash (cf. succinimide, p. 245) and melts at 238° . It is important for making anthranilic acid (p. 414) for indigo.

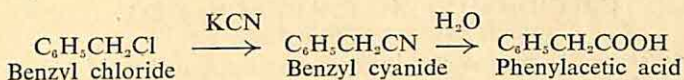


Tests for phthalic acid.—(i) On fusing with phenol and concentrated H_2SO_4 , phthalic acid or its anhydride forms phenolphthalein which gives a pink colour with dilute caustic soda solution. (ii) On repeating test (i) with resorcinol in place of phenol, a reddish solution with an intense green fluorescence is obtained, due to the formation of fluorescein.

Isophthalic acid (m.p. 346°) may be prepared by the oxidation of *m*-xylene with nitric acid or *m*-toluic acid with alkaline pot. permanganate. **Terephthalic acid** is obtained similarly from *p*-xylene. None forms inner anhydride or gives the fluorescence test as the *o*-compound. Both are insoluble in water, the barium salt of the iso-acid (but not of terephthalic acid) dissolves in water. Both sublime undecomposed on heating. They are identified by their methyl esters —methyl isophthalate melts at 65° but methyl terephthalate at 140° . By perature, a synthetic polyester fibre, called *Terylene* in U.K. and *Dacron* in U.S.A., resembling Nylon, is now manufactured. It melts at 249° , is inflammable but quite strong and resistant to light and bacteria. It is only slightly hygroscopic, it dries very rapidly.

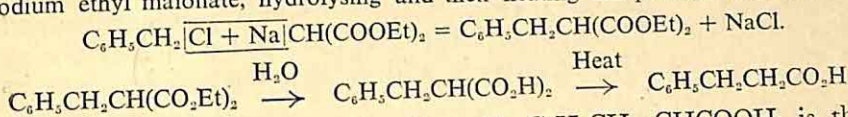
Aromatic acids with $-\text{COOH}$ in the side-chain resemble the aliphatic and may be regarded as such, a H-atom of the alkyl group having been replaced by an aryl radical. They are also similarly prepared, e.g., by oxidising the corresponding aldehydes and alcohols, by hydrolysing the respective nitriles, etc.

Phenylacetic acid, $C_6H_5CH_2COOH$, is formed when some proteins putrify; it may be readily obtained by boiling benzyl chloride with aqueous-alcoholic pot. cyanide for about three hours, and hydrolysing the benzyl cyanide formed with boiling dilute sulphuric acid.



Phenylacetic acid crystallises in glistening, colourless plates (m.p. 76°). It has a very foul odour, but its ethyl ester is a perfume. Chromic acid or alkaline pot. permanganate oxidises it to benzoic acid. The isomeric toluic acids, $C_6H_4(CH_3)COOH$, yield phthalic acids on oxidation. The halogen atom enters the nucleus or the side-chain according as halogenation is done in the cold in presence of a halogen carrier, or at the boiling temperature. Phenylacetic acid is stronger ($k = 6.0 \times 10^{-5}$) than acetic acid. It is added to fermentation medium to stimulate the yield of benzylpenicillin.

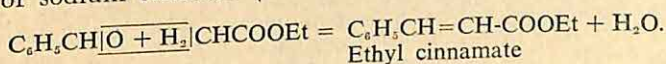
β -Phenylpropionic acid, $C_6H_5CH_2CH_2COOH$, is a crystalline solid. (m.p. 46°), soluble in hot water; it is prepared by reducing cinnamic acid, $C_6H_5CH=CH.CO_2H$, with sodium amalgam or condensing benzyl chloride with sodium ethyl malonate, hydrolysing and then heating the product formed:



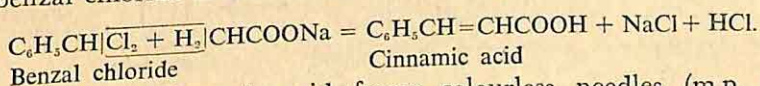
Cinnamic acid, β -phenylacrylic acid, $C_6H_5CH=CHCOOH$, is the most important aromatic unsaturated acid. It occurs free and as benzyl ester in Peru and Tolu balsams and in storax. It may be obtained therefrom by boiling with caustic soda and decomposing the sodium salt with hydrochloric acid. It is usually made by Perkin's reaction (p. 403):

Benzaldehyde (20 c.c.), fused sodium acetate (10 g.) and acetic anhydride (30 c.c.) are heated in a flask fitted with an air-condenser for about eight hours to 180° in an oil-bath. The hot mixture is poured into water (100 c.c.) and made alkaline with sodium carbonate; unchanged benzaldehyde is removed by steam-distillation. The filtered solution is acidified to precipitate cinnamic acid; it is recrystallised from boiling water or light petroleum.

Benzaldehyde may also be condensed with fatty acid esters in presence of sodium ethoxide (Claisen's reaction, p. 404);

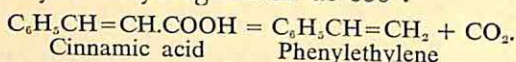


Commercially, cinnamic acid is made by heating sodium acetate and benzal chloride to 200° in an autoclave (p. 343).

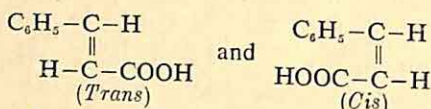


Properties.—Cinnamic acid forms colourless needles (m.p. 133°) and resembles acrylic acid (p. 236). Sodium amalgam reduces it to β -phenylpropionic or hydrocinnamic acid. It adds up bromine and also decolorises alkaline permanganate, forming β -phenylglyceric acid, $C_6H_5CHOH.CHOH.CO_2H$. Cinnamic acid is readily oxidised to benzoic acid. Distilled alone or with soda-lime, it gives phenylethylene or *styrene*—a pleasant-smelling liquid (b.p. 145°) which readily polymerises at ordinary temperature in presence of peroxides to a trans-

parent thermoplastic resin, *polystyrene*. It is a good electrical insulator. Styrene is manufactured from ethylbenzene (made from benzene and ethylene) by catalytic dehydrogenation at 630° .

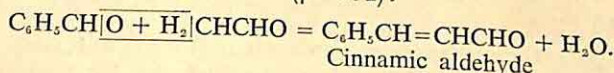


Theory demands two isomeric forms of cinnamic acid (*cf.*, fumaric and maleic acids, p. 250) *viz.*



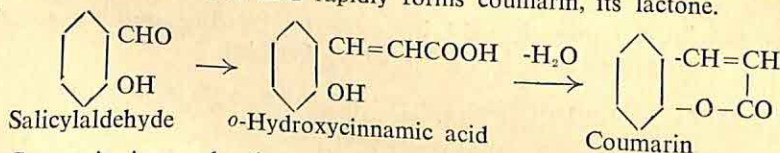
But six are known. The naturally-occurring or synthetic acid is the *trans*-form having two crystalline modifications, α - (diamond-shaped) and β - (needle-like); both melt at 133° . The α -form is more stable than the β -. The *cis*-form, *allo-cinnamic acid*, has four crystalline modifications (melting at 32° , 42° , 58° and 68°), obtained by exposing cinnamic acid to ultra-violet light. These are mutually convertible and chemically alike. They are all labile, the most stable of them being the one with m.p. 68° . Cinnamic acid is used in medicine, and its esters in perfumery.

Cinnamic aldehyde, $\text{C}_6\text{H}_5\text{CH}=\text{CHCHO}$, is the main constituent of oil of cinnamon (50-65%) and cassia oil (10-85%) from which it may be extracted as the bisulphite-compound. It is prepared by Claisen's reaction by condensing benzaldehyde with acetaldehyde in presence of sodium ethoxide or caustic soda (p. 404):



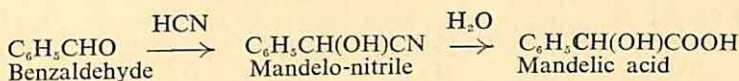
Cinnamic aldehyde is a yellow oil (b.p. 246°), having the fragrant odour of cinnamon. It is readily oxidised to cinnamic acid by air. Strong acids convert it into a resin. It has some use in perfumery.

Coumarin has two condensed rings, and is heterocyclic. It is the inner ester (or lactone) of *o*-hydroxycinnamic or coumaric acid; it is present in sweet woodruff, newly mown hay and tonka bean (called *cumaru* by South Americans). It is made from salicylaldehyde, sodium acetate and acetic anhydride by Perkin's reaction (*cf.*, preparation of cinnamic acid, p. 421) and was first obtained by Perkin. The acid rapidly forms coumarin, its lactone.



Coumarin is a colourless, crystalline solid (m.p. 67°) with a sweet odour. It is soluble in alcohol, ether and hot water. It is used in perfumery, and also as a *fixative* for perfumes. It is no longer employed for flavouring foods and drinks because of its toxicity. *o*-Hydroxycinnamic acid (*trans*-form) is odourless.

Mandelic acid, $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{COOH}$, the simplest of hydroxy-aromatic acids having both -OH and -COOH in the side-chain, is isomeric with hydroxytoluic acids. It is made by hydrolysing the cyanhydrin of benzaldehyde or mandelonitrile (p. 402) and was first obtained by heating bitter almond (German *mandel*, almond) with hydrochloric acid.



Mandelic acid (m.p. 133°), having an asymmetric C-atom (in bold type), is optically active. It resembles lactic acid (p. 189). It is fairly soluble in water. On oxidation, benzoylformic acid, $\text{C}_6\text{H}_5\text{COCOOH}$, and on reduction, phenylacetic acid, $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$, result. The acid is an antiseptic for the urinary tract, and also a perfume.

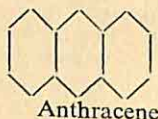
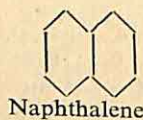
QUESTIONS

- Starting with benzene, show schematically how you would prepare benzoic acid, aniline, phenol and benzyl alcohol. Show how benzene may be obtained from these substances.
B.Sc. Pass, 1938, Dacca Uni.
- How is salicylic acid manufactured? Describe its properties & uses, and show how you will prepare its methyl and ethyl ester.
B.Sc., 1951, Gauhati Uni.; B.A., B.Sc. Pass, 1933, Allahabad Uni.
- How would you effect the separation of an aromatic acid and a phenol?
B.Sc., 1928, Punjab Uni.
- How may hydrogen in benzene be replaced by $-\text{OH}$, $-\text{CH}_3$, $-\text{NH}_2$, $-\text{NO}_2$ and $-\text{COOH}$ groups?
B.A. & B.Sc., Pass, 1932, Allahabad Uni.
- What is mandelic acid? How can this be prepared? What are its properties? Compare mandelic acid with lactic acid so far as the action of (i) HNO_3 , (ii) HI , and (iii) HCl on both these compounds is concerned.
B.Sc. 1945, Nagpur Uni.
- Describe the preparation, properties and uses of the following: cinnamic acid, benzoyl chloride, aspirin, methyl salicylate and phthalic anhydride.
- Indicate by means of formulæ and reactions how you would distinguish by simple chemical means between: (a) *p*-bromotoluene and benzyl bromide, (b) ethylbenzene and *m*-xylene, (c) benzamide and acetanilide, and (d) methyl ether of salicylic acid and methyl ester of salicylic acid.
B.Sc. Degree Exam. 1942, Annamalai Uni.
- Give brief experimental details for the preparation of the following in a pure condition: (a) salicylaldehyde, (b) phenylhydrazine, (c) cinnamic acid, (d) malachite green.
B.Sc. Degree Exam. 1941, Travancore Uni.
- Describe the preparation of salicylic acid. By what tests would you distinguish between (a) salicylic and benzoic acid, (b) salicylic acid and phenol?
B.Sc. Pass, 1952, Nagpur Uni.; B.Sc. 1946, Benares Hindu Uni.
- A colourless fuming liquid **A** contains 59.79% C, 3.56% H and 25.27% Cl and has a vapour density of 0.0063 g. per c.c. at N.T.P. With ammonia, it forms **B** which with boiling NaOH gives NH_3 and the sodium salt of a monobasic acid **C** (mol. wt. 122). What are **A**, **B** and **C**?
Ans. $\text{C}_6\text{H}_5\text{COCl}$, $\text{C}_6\text{H}_5\text{CONH}_2$, $\text{C}_6\text{H}_5\text{COOH}$.

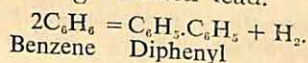
CHAPTER XLII

THE MULTINUCLEAR COMPOUNDS

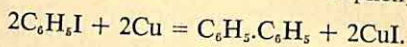
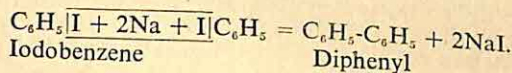
Organic compounds, containing two or more benzene nuclei are called *polycyclic* or *multinuclear compounds* which are important in making dyes. They are mainly of two types according as the rings are distinct or condensed. In the former, the rings may be linked either directly or through a carbon chain, *e.g.*, diphenyl, $\text{C}_6\text{H}_5\text{-C}_6\text{H}_5$, and diphenylmethane, $\text{C}_6\text{H}_5\text{-CH}_2\text{-C}_6\text{H}_5$. In the latter, two carbon atoms are common to adjacent rings, *e.g.*, naphthalene and anthracene.



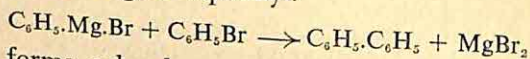
Diphenyl, biphenyl, $\text{C}_6\text{H}_5\text{-C}_6\text{H}_5$, the simplest of multinuclear hydrocarbons, occurs in coal-tar. It may be regarded as derived from benzene by replacing a H-atom by a phenyl group. Diphenyl is manufactured by passing benzene vapour through a red-hot tube ($600^\circ\text{-}800^\circ$) packed with pumice, or through molten lead.



More easily it can be prepared in the laboratory by reacting iodobenzene with sodium in dry ethereal solution (Fittig's method, p. 327), or heating iodobenzene with copper powder at 220° in a sealed tube (*Ullmann reaction*). It recalls the formation of ethane from methyl iodide (p. 44).



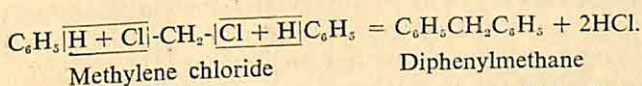
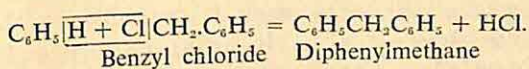
Phenylmagnesium bromide and bromobenzene react in presence of cobaltous chloride to give diphenyl.



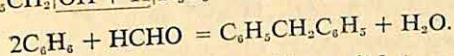
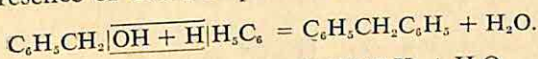
Diphenyl forms colourless plates (m.p. 71° , b.p. 254°), readily soluble in alcohol or ether. It can be sulphonated, nitrated or halogenated. The phenyl group directs substituents to the *p*-position chiefly and to the *o*-position to some extent. With chromic acid, it gives mainly carbon dioxide and water, and only a little benzoic acid. Its diamino-derivative, benzidine (p. 373), is technically important, and is derived from nitrobenzene. Diphenyl impregnated wrapping paper prevents rotting of citrus fruits. It is also employed as a heat-transfer medium in place of steam in chemical engineering due to its great stability above its b.p.—boilers operate at high temperature under low pressure. The benzene rings in diphenyl lie along the same axis, *i.e.*, the molecule is symmetrical (one ring is not folded on the other giving

the "butterfly" formula) as *pp'*-dichlorodiphenyl has zero dipole moment. The crystal structure of *pp'*-diphenyl derivatives has a centre of symmetry; this is possible only if the benzene rings are co-axial.

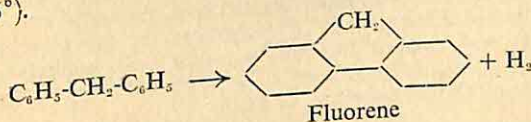
Diphenylmethane, $\text{C}_6\text{H}_5\text{-CH}_2\text{-C}_6\text{H}_5$, is usually prepared by reacting benzene and benzyl chloride (or methylene chloride) in presence of aluminium chloride (Friedel-Crafts).



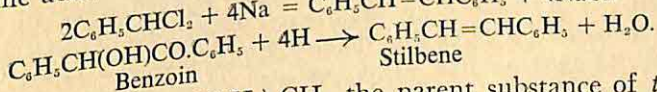
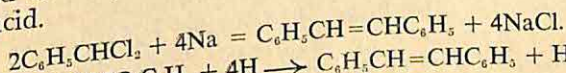
It is also formed when benzyl alcohol or formaldehyde reacts with benzene in presence of conc. sulphuric acid.



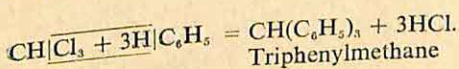
Diphenylmethane is a white, crystalline solid (m.p. 26° , b.p. 262°), soluble in alcohol and ether. Chromic acid oxidises it to benzophenone, $\text{C}_6\text{H}_5\text{CO}\cdot\text{C}_6\text{H}_5$ (p 406), which can be reduced back to diphenylmethane. In presence of catalysts, chlorine enters the *p*-position of both the rings of diphenylmethane, but in sunlight, diphenyldichloromethane, $\text{C}_6\text{H}_4\text{CCl}_2\text{C}_6\text{H}_4$, is formed. During nitration, the -NO_2 group goes mainly to the *p*-position of each ring. For its geranium-like smell, diphenylmethane is used for perfuming soap. Passed through a red-hot iron tube, it forms diphenylenemethane or *fluorene*, a colourless solid (m.p. 115°).



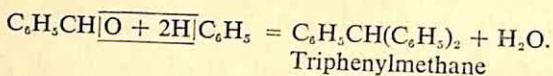
s-Diphenylethylene, $\text{C}_6\text{H}_5\text{CH=CHC}_6\text{H}_5$, occurs in *cis-trans* forms; the stable *trans*-isomer is called stilbene (m.p. 124°); iso-stilbene (b.p. 145°) is the *cis*-form. Stilbene may be obtained by heating benzal chloride and metallic sodium, or by reducing benzoin. Some stilbene derivatives are used in medicine; most of the fluorescent whitening agents applied to undyed fabrics today are based on diamino-stilbene-disulphonic acid.



Triphenylmethane, $(\text{C}_6\text{H}_5)_3\text{CH}$, the parent substance of *triphenylmethane dyes*, is obtained: (1) By warming chloroform (or benzal chloride, $\text{C}_6\text{H}_5\text{CHCl}_2$), benzene and aluminium chloride together (Friedel-Crafts).



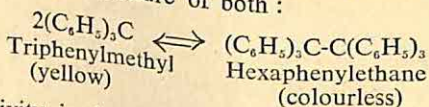
(2) By condensing benzaldehyde and benzene in presence of zinc chloride at about 270°.



Triphenylmethane is a colourless, crystalline solid (m.p. 92°, b.p. 359°), slightly soluble in cold alcohol, but readily soluble in ether, hot alcohol and benzene. From benzene, it crystallises with a molecule of the solvent, and melts at 75°. It forms molecular compounds with aniline, thiophene, etc. The H of the tertiary carbon is acidic due to the presence of three phenyl groups, and can be replaced by sodium or potassium, giving triphenyl methyl sodium, $(\text{C}_6\text{H}_5)_3\text{C}^-\text{Na}^+$. PbO_2 or chromic acid oxidises it to triphenylcarbinol, $(\text{C}_6\text{H}_5)_3\text{C.OH}$, (m.p. 165°) which behaves as a weak base, forming an unstable sulphate and a chloride with H_2SO_4 and HCl respectively. Triphenylmethyl chloride, $(\text{C}_6\text{H}_5)_3\text{CCl}$, behaves as a strong electrolyte in liquid sulphur dioxide solution due to ionisation as $(\text{C}_6\text{H}_5)_3\text{C}^+$ and Cl^- .

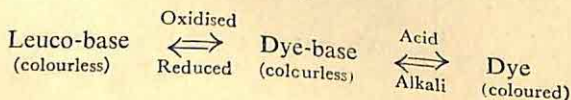
Tetraphenylmethane, $(\text{C}_6\text{H}_5)_4\text{C}$, a very stable, crystalline solid (m.p. 282°, b.p. 431°), is obtained in poor yield by reacting triphenylmethyl chloride with phenylmagnesium bromide. Benzene in excess and carbon tetrachloride in presence of aluminium chloride give triphenylmethyl chloride but *not* tetraphenylmethane.

Triphenylmethyl, $(\text{C}_6\text{H}_5)_3\text{C}$.—On heating triphenylmethyl chloride, $(\text{C}_6\text{H}_5)_3\text{CCl}$, in benzene solution with finely divided silver, in an atmosphere of carbon dioxide, M. Gomberg (1900) obtained a highly reactive crystalline compound. Theoretically, hexaphenylethane, $(\text{C}_6\text{H}_5)_3\text{C}-\text{C}(\text{C}_6\text{H}_5)_3$, ought to result. The compound readily absorbed oxygen from the air to form a peroxide, and combined with halogens to give halides. Mol. wt. determination in benzene by ebullioscopic method gave 383 which lies between the values for triphenylmethyl (243) and hexaphenylethane (486). The existence of the free radical, triphenylmethyl, $(\text{C}_6\text{H}_5)_3\text{C}$, was proved for the first time (cf., methylene, p. 56). It is highly reactive and readily passes on to hexaphenylethane. The compound of Gomberg is an equilibrium mixture of both :



The high reactivity is due to the unsaturated character of triphenylmethyl having a trivalent C-atom. Trinaphthylmethyl, $(\text{C}_{10}\text{H}_7)_3\text{C}$, however, remains in the unimolecular form entirely, and does not form hexanaphthylethane.

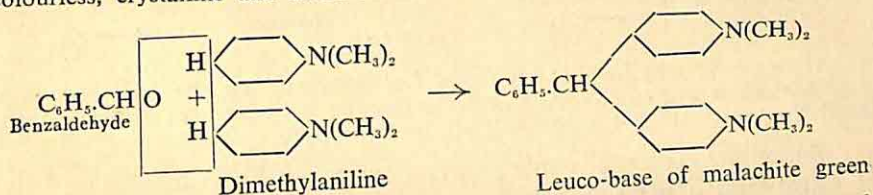
The triphenylmethane dyes.—If amino, substituted amino or hydroxyl groups be introduced into the para-position of the benzene nuclei with respect to the methane-carbon of triphenylmethane, *leuco-compounds* of triphenylmethane dyes or leuco-bases are obtained. Leuco-bases (*leukos*, white) are *colourless*; on oxidation, they produce the dye-bases which are also *colourless*. These are derivatives of triphenylcarbinol or its homologue. The dyes are obtained from the dye-bases by salt-formation with acids:



This salt-formation invariably takes place with the elimination of water, resulting in the formation of a *quinonoid structure*, $=\langle \text{C}=\text{C} \rangle=$, which is the *chromophore* (p. 374) in these dyes; $-\text{NH}_2$ and $-\text{OH}$ groups are the *auxochromes* (p. 374). These changes will be illustrated in the case of malachite green. Triphenylmethane dyes which are usually basic, give brilliant shades but are not quite fast.

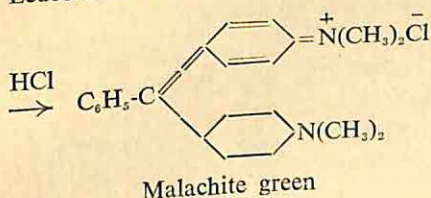
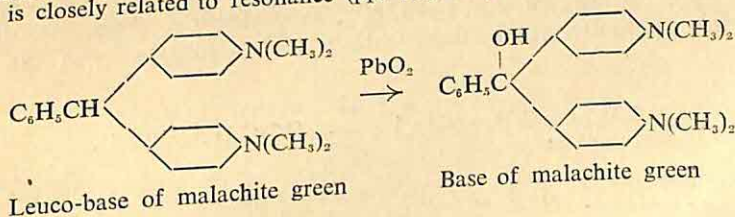
Malachite green or *benzaldehyde green* was discovered in 1877 by O. Fischer, whose method is still followed for its manufacture. It is prepared from benzaldehyde and dimethylaniline. The three steps of formation *viz.*, leuco-base, dye-base and dyestuff are:

(i) *Leuco-base*: Benzaldehyde (1 mol.) and dimethylaniline (2 mols.) are heated to about 100° with solid zinc chloride (or conc. HCl). The aldehyde condenses with two mols. of dimethylaniline in the *p*-position to form tetramethyldiaminotriphenylmethane, the leuco-base of malachite green. The water formed is taken up by zinc chloride or hydrochloric acid. The leuco-base is colourless, crystalline and insoluble in water.



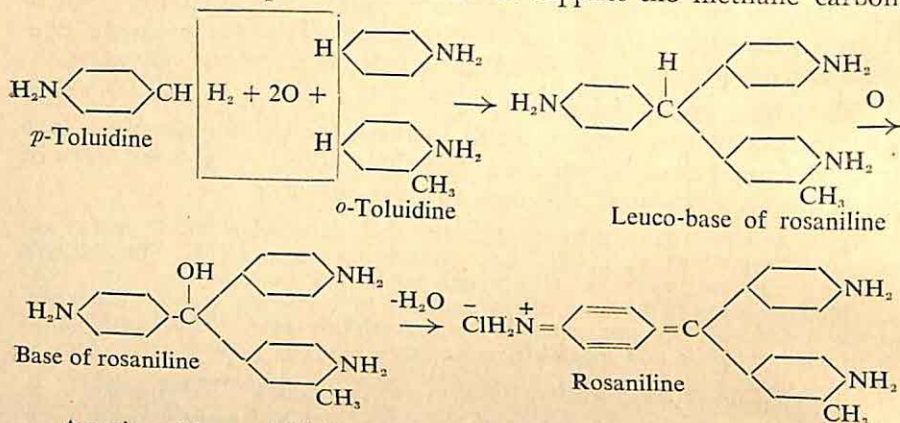
(ii) *Dye-base*: The leuco-base is oxidised with lead peroxide, PbO_2 , and HCl at $0^\circ\text{--}5^\circ$ to the corresponding carbinol or dye-base. This also is colourless and insoluble in water.

(iii) *Dyestuff*: The dye-base dissolves in hydrochloric acid as the hydrochloride. This, on warming, loses water and forms malachite green, usually represented by the quinonoid structure. The intense colour of triphenylmethane dyes is closely related to resonance (pp. 106, 324).



Malachite green, a basic dye, dyes silk, wool, jute etc., directly a bright green. It dyes cotton mordanted with tannin. It is also used for dyeing leather, paper, oils, acetate rayon, etc. Malachite green usually comes to the market as the oxalate. It is a germicide. Basic dyes are cheap, but not fast to light.

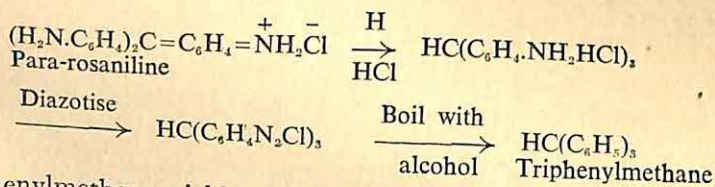
Rosaniline, *magenta* or *fuchsine* is one of the oldest synthetic dyes, discovered by Verguin in 1859. It is usually prepared by oxidising a mixture of equal parts of aniline, *o*- and *p*-toluidine with nitrobenzene. Here the *p*-toluidine molecule supplies the methane carbon.



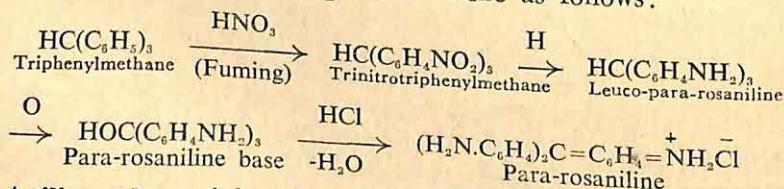
Arsenic acid was initially employed for oxidation, but the last traces of arsenic which is a poison, could not be removed. Nitrobenzene, HCl and iron filings have now replaced it, the latter two are catalysts.

Rosaniline forms glistening, green crystals which dissolve readily in water with a deep red colour. It dyes silk and wool directly, and also cotton, mordanted with tannin, a brilliant red. It is used for colouring foods. On passing sulphur dioxide into its aqueous solution, magenta is reduced to the leuco-base which is colourless. This is *Schiff's reagent* for aldehydes (p. 130).

Para-rosaniline is prepared, like rosaniline, by oxidising *p*-toluidine (1 mol.) and aniline (2 mols.) with nitrobenzene. Its salts are soluble in warm water; they dye silk, wool, etc., as rosaniline. Para-rosaniline forms triphenylmethane on diazotisation and treatment with boiling alcohol:



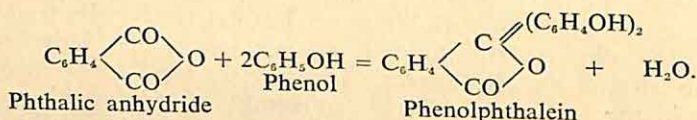
Triphenylmethane yields para-rosaniline as follows:



Aniline blue, triphenyl-para-rosaniline or spirit blue is prepared by heating para-rosaniline base with excess of aniline in presence of a little benzoic or acetic acid, to about 180°:

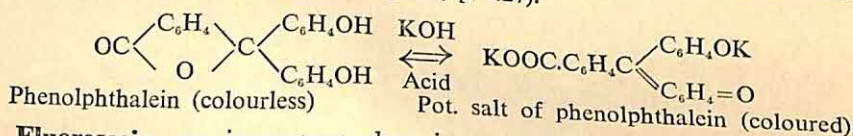
The **phthaleins** are triphenylmethane derivatives, formed on heating phthalic anhydride with phenols. The para-hydrogen atoms of two phenol molecules combine with the carbonyl oxygen of phthalic anhydride; the water formed is taken up by a dehydrating agent. The phthaleins are colourless, but with alkalis, they form coloured salts having a quinonoid structure. The simplest of the phthaleins is phenolphthalein which is not a dye but related to phthalein dyes.

Phenolphthalein is prepared by heating to 120° phthalic anhydride (30 g.) and phenol (40 g.) for about eight hours in presence of anhydrous zinc chloride (50 g.) or conc. sulphuric acid (p. 388). The mass is treated with caustic soda solution when a deep pink solution of the sodium salt is formed. Phenolphthalein is precipitated therefrom by acids. It is purified by recrystallisation from aqueous alcohol.

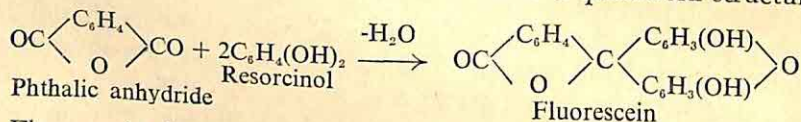


Phenolphthalein forms white crystals (m.p. 258°), sparingly soluble in water but readily soluble in dilute alkalis with a deep pink colour which vanishes on acidification. It is an indicator (pH range 8.3-10.0). With excess of conc. caustic alkali, phenolphthalein gives a *colourless* solution; trisodium salt of the carbinol form, $(\text{NaO.C}_6\text{H}_4)_2\text{C}(\text{OH}).\text{C}_6\text{H}_4\text{COONa}$, results and the quinonoid structure disappears. It is a purgative in medicine.

Formation of deeply coloured salts from phenolphthalein is associated with a quinonoid structure (cf., malachite green, p. 427).



Fluorescein, an important dye, is prepared by heating phthalic anhydride with resorcinol to about 200° (p. 394), no condensing agent like zinc chloride or sulphuric acid is necessary. The dark mass formed is extracted with dilute caustic soda and fluorescein precipitated with hydrochloric acid. It is believed to have a quinonoid structure.



Fluorescein is a dark-red powder, readily soluble in alcohol but insoluble in water. The solution in alkali, on dilution with a large volume of water, exhibits an intense yellowish-green fluorescence, hence the name. Resorcinol, pyrogallol and phthalic anhydride are usually detected by this reaction. The disodium salt is the *uranine* of commerce. Fluorescein dyes silk and wool yellow, but the colour is fugitive. It is employed in eye surgery and in making eosin dyes. Air troops carried fluorescein during the last war to dye the sea water with in case of wreck; this made location by rescuing planes easy.

Eosin or tetrabromofluorescein is made by brominating fluorescein in alcohol. Two H-atoms of each resorcinol nucleus are thus substituted by bromine. Eosin separates as red crystals, insoluble in water but soluble in alcohol. It shows greenish-red fluorescence in high dilution. The sodium salt of tetrabromofluorescein is the eosin of commerce. It dyes wool, mordanted cotton, and silk a bright pink. The dye is fast. It is largely used in making red ink, and also as a biological staining material.

Erythrosin, sodium salt of tetraiodofluorescein, is a dye for foods. **Mercurochrome**, a mercury derivative of dibromofluorescein, is a powerful antiseptic (a 2% solution in water is generally used); it is a deep red solid, soluble in water.

QUESTIONS

1. Write an essay on the triphenylmethane dyes. B.Sc. Degree Exam. 1942, Travancore Uni.
2. How are any three of the following prepared? (a) eosin, (b) phenolphthalein, (c) malachite green, (d) rosaniline.
3. How is triphenylmethane prepared? Indicate its importance with respect to the group of dyes known as triphenylmethane colours. B.Sc. Exam, 1947, Bombay Uni.
4. Give the structural formula and one method of preparation of each of the following: fluorescein, malachite green. A.I.C. 1935.
5. Write what you know about free radicals. How is triphenylmethyl obtained?
6. How is phenolphthalein prepared? Discuss its use as an indicator.
7. Write an essay on the relation between colour and constitution of organic substances. B.Sc. Hons. 1932, Dacca Uni.
8. Describe the preparation, properties and uses of any four of the following: chloroform, hexamine, iodobenzene, benzoyl chloride and phenolphthalein. B.Sc. Pass, 1942, Patna Uni.
9. Indicate how the following substances are prepared: (a) pararosaniline, (b) eosin, and (c) aurin.
10. How is malachite green prepared? What is the cause of its colour? B.Sc. Pass, 1951, Nagpur Uni.

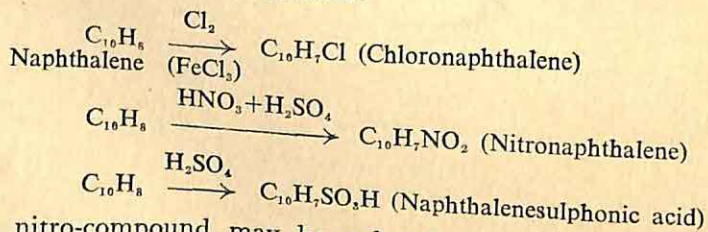
CHAPTER XLIII

NAPHTHALENE AND ITS DERIVATIVES

Naphthalene, $C_{10}H_8$, next to benzene in commercial importance, was discovered in coal-tar by Garden in 1819. Due to its high volatility, it deposited in the condensers during distillation of crude naphtha and was called naphthalene. It occurs in the middle oil fraction of coal-tar (p. 318) and is invariably obtained therefrom. It represents 5-10% of the tar, and is the largest single constituent. On cooling the middle oil, most of the naphthalene crystallises and is separated by pressing out the oil in a hydraulic press. The crude product is washed with caustic soda solution to remove the adhering phenols and warmed with a little conc. sulphuric acid which forms soluble salts and sulphonic acids with the impurities. Naphthalene is purified by sublimation. A second crop is obtained by the fractional distillation of the mother-liquor after removing phenol with caustic soda solution. Crude naphthalene contains thionaphthene, C_8H_6S , as coal-tar benzene has thiophene. The tar from low temperature carbonisation of coal contains no naphthalene. Many hydrocarbons such as methane, ethane, acetylene, benzene, etc., when passed through red-hot tubes, are partially converted into naphthalene. It occurs in some petroleums and essential oils.

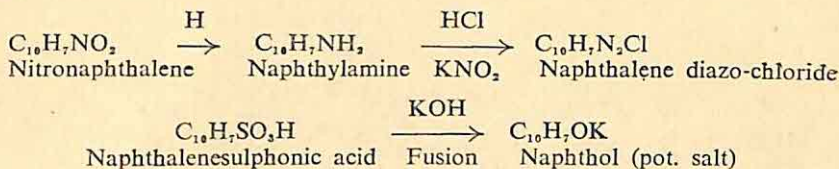
In 1955 U.S.A. produced 477 million lb. of naphthalene (70% being used for making phthalic anhydride). India's annual production is only 1·80 million lb.

Properties.—Naphthalene forms large, white, shining plates (m.p. 80° , b.p. 218°). It has a characteristic, but not unpleasant, smell and is volatile at all temperatures; naphthalene accompanies coal-gas and causes trouble in the pipes or purifiers. It is insoluble in water but dissolves readily in benzene, ether and hot alcohol. It burns with very luminous flame depositing much soot, and is volatile in steam. Naphthalene resembles benzene but is more reactive; it can be halogenated, nitrated or sulphonated—the products behave like the corresponding derivatives of benzene:



The nitro-compound may be reduced to amino-, and the latter diazotised in the usual manner. The sulphonic acid, on potash fusion, yields a hydroxy-compound. The -OH group, linked to a carbon atom

of the nucleus, endows the compound with phenolic properties, and so on.

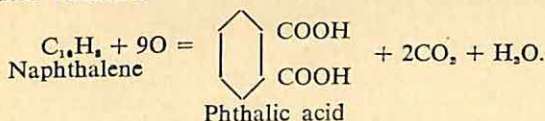


Naphthalene, when added to picric acid (both in strong alcoholic or acetone solution), forms long, golden yellow needles of naphthalene picrate, $\text{C}_{10}\text{H}_8 \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$, (m.p. 149°) by which it may be identified and also estimated. The picrate decomposes on boiling with alcohol, or treatment with alkalis. Naphthalene combines with metallic sodium in dry methyl ether to form two disodium addition products (1:2 & 1:4) which take up CO_2 and yield two dihydronaphthalene-dicarboxylic acids (as sodium salts).

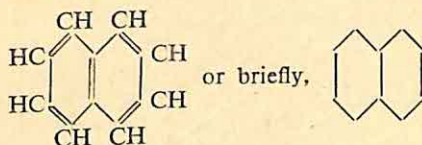
Uses.—Naphthalene is largely used in making dyestuffs such as azo-dyes, indigo, eosin, etc. and also decalin, tetralin, phthalic acid, etc. It is a common insecticide, a moth repellent (*moth balls*), but not a powerful antiseptic. It increases the illuminating power of coal-gas.

Constitution.—(i) The molecular formula of naphthalene is C_{10}H_8 ; it has aromatic properties and resembles benzene.

(ii) On heating to about 300° with conc. H_2SO_4 in presence of mercury, it is oxidised to phthalic acid, $\text{C}_6\text{H}_4(\text{COOH})_2$. Naphthalene is, therefore, an ortho-substituted benzene.

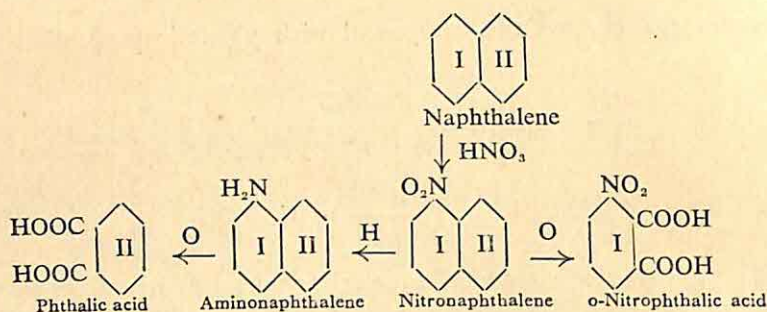


(iii) Erlenmeyer (1866) suggested the following structure for naphthalene by analogy to that of benzene proposed by Kekulé a year earlier.



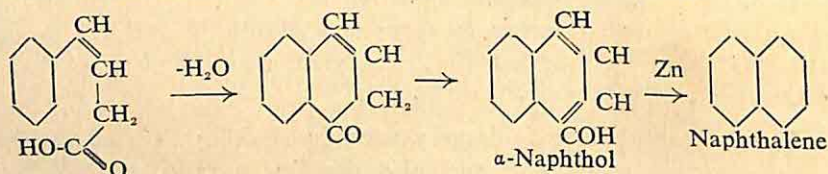
(iv) The fusion of two benzene nuclei in *o*-position was established by Graebe (1869) as follows:

Mononitronaphthalene, $\text{C}_{10}\text{H}_7\text{NO}_2$, yields, on oxidation, *o*-nitrophthalic acid; so a benzene nucleus with a nitro group in nitronaphthalene remains intact. But if nitronaphthalene is reduced to aminonaphthalene, $\text{C}_{10}\text{H}_7\text{NH}_2$, and then oxidised, phthalic acid is obtained. The benzene ring with the amino group has disappeared; a second nitrogen-free benzene ring gives the phthalic acid. The nitro group deactivates the nucleus which resists oxidation while the amino group activates it and helps oxidation.



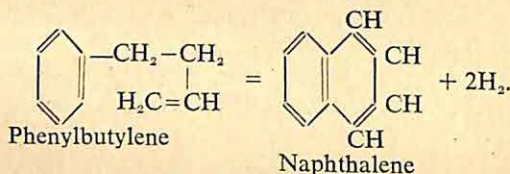
(v) The Erlemeyer constitution has been confirmed by several syntheses :

(a) β -Benzylidenepropionic acid forms α -naphthol on heating to about 300° . The latter, on distillation with zinc dust, yields naphthalene (Fittig) :

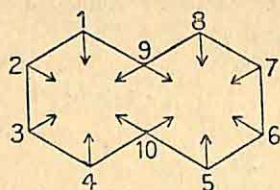


β -Benzylidenepropionic acid

(b) Phenylbutylene or its dibromide forms naphthalene on passing over red-hot soda-lime or calcium oxide :

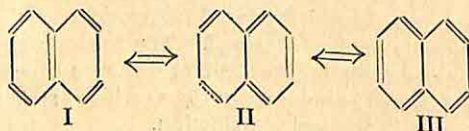


The fourth valency of carbon is a problem as in benzene. Bamberger proposed a centric formula for naphthalene, corresponding to that of Armstrong and Baeyer for benzene. Harries (1905) suggested a centric formula for one nucleus and a Kekulé ring for the other to explain the behaviour of naphthalene during oxidation and reduction.



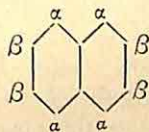
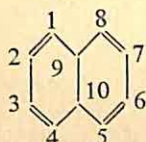
Naphthalene (Bamberger)

As in benzene, the double bonds may have different positions, and naphthalene may be represented by



A resonance hybrid (p. 324) which is an average of these three, adequately explains its behaviour. Naphthalene is more reactive than benzene, e.g., unlike benzene, it is reduced to tetrahydronaphthalene by sodium and hot alcohol, and forms the tetrachloride with chlorine in absence of light. The resonance structure accounts for this difference. If all the three forms (I, II & III) contribute *equally*, the bond between carbon 1 and 2 (see below) has $\frac{2}{3}$ double bond character in contrast with $\frac{1}{2}$ double bond character for each bond in benzene. Hence addition takes place there more readily than in benzene. For a similar reason, the bond between carbon 2 and 3 has only $\frac{1}{3}$ double bond character, and is consequently less reactive than the bond between carbon 1 and 2. It behaves more like a single bond compared to bonds in benzene. The bonds in naphthalene, unlike those in benzene, are neither equivalent nor of equal length. The bond lengths in naphthalene are C_1-C_2 , 1.35Å; C_2-C_3 , 1.40Å; C_1-C_9 , 1.42Å, C_9-C_{10} , 1.40Å.

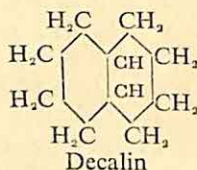
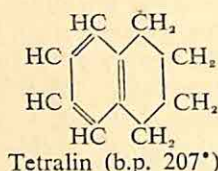
Isomerism of naphthalene derivatives.—The substitution products of naphthalene are more numerous than those of benzene. In order to distinguish them, the C-atoms linked to hydrogen are numbered or indicated by Greek letters. The H-atoms form two groups of four each, which are symmetrical.



Due to symmetry of the molecule, the positions 1, 4, 5 and 8 (denoted by α) are equivalent as also the positions 2, 3, 6 and 7 (denoted by β). But none of the latter positions is similar to any of the former. This means that each mono-substituted naphthalene should exist in two isomeric forms, α - and β -, which is a fact. By replacing a H by an -OH, we obtain two naphthols, α - and β -. Similarly, ten di- and fourteen tri-substituted naphthalenes are theoretically possible. All the ten dichloronaphthalenes are known. This number becomes greater still if the substituents are different— 14 di- and 84 tri-derivatives are possible. If both the substituents are in the same ring, they are sometimes called ortho-, meta- and para- derivatives; if in different rings, they are usually denoted by numbers, e.g., 4:5- or $\alpha\alpha$ -dibromonaphthalene. The position 1:8 (or 4:5) is called *peri*-position (Greek *peri* near), it is similar to ortho-position; 2:6 or 3:7 position is known as *amphi* (*amph* on both sides). In naphthalene, the substitution readily occurs in the α -position which is more reactive.

Hydrogenated naphthalenes.—Naphthalene is more readily reduced than benzene (see above). Under suitable conditions, it can take up 2, 4, 6, 8 or 10 hydrogen atoms. Of these, tetrahydronaphthalene or *tetralin*, $C_{10}H_{12}$, and decahydronaphthalene or *decalin*, $C_{10}H_{18}$, are important. They are made from naphthalene with hydrogen at 10-15 atmos. pressure in presence of finely divided nickel (Sabatier); at 120°-150°, decalin is formed, but at 150°-200°, tetralin is the main product. They are chiefly employed for making lacquers, and also as

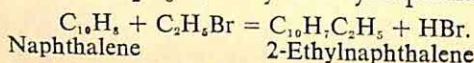
turpentin: substitutes in boot-creams. Mixed with benzene and alcohol, they serve as motor fuel. They are good solvents for resins and fats.



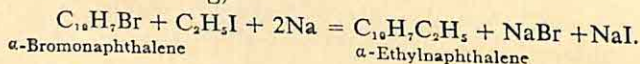
Decalin is more expensive, but no better, than tetralin which is more widely used. In tetralin all the 4 H-atoms have entered the *same* ring which consequently behaves as a hydroaromatic compound while the other is now a typical benzene ring. The hydrogenation of the second ring is rather difficult. Decalin exists in two forms, *cis* and *trans* (b.p. 193° and 185° respectively) with respect to the two central H-atoms, corresponding to the 'bed' and 'chair' forms (p. 312). With nickel catalyst, the *trans* form is the main product but with platinum, the *cis* form predominates.

Homologues of naphthalene.—Methyl- and ethyl-naphthalenes occur in traces in coal-tar and certain petroleum, and are obtained therefrom commercially. Homologues of naphthalene may be prepared like those of benzene.

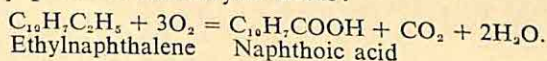
(i) Naphthalene, with alkyl iodide in presence of aluminium chloride, yields alkylnaphthalene (*Friedel-Crafts*) at low temperature; at high temperature, the ring is broken. With CH_3I , 1- and 2-methylnaphthalene and with $\text{C}_2\text{H}_5\text{Br}$, only 2-ethylnaphthalene are formed.



(ii) Bromonaphthalene produces alkylnaphthalene with alkyl iodide and sodium (*Wurtz-Fittig*):



These behave like the homologues of benzene; for example, on oxidation, they produce carboxylic acids:



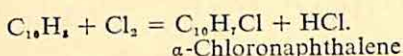
α -Methylnaphthalene is a liquid (b.p. 242°) while the β -isomer is a solid (m.p. 32°). Methylnaphthalenes are standard high-knocking fuel for Diesel engines; their sulphonates are wetting agents in the textile industry.

Halogen derivatives of naphthalene.—As with benzene, two types of halogen derivatives are possible with naphthalene—additive and substitutive. These are of little importance, theoretically or commercially.

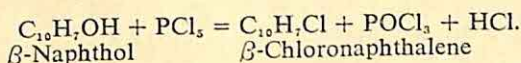
Naphthalene dichloride, $\text{C}_{10}\text{H}_8\text{Cl}_2$, a yellow, oily liquid, is obtained by treating naphthalene in CHCl_3 with dry Cl_2 at room temperature. It is unstable and decomposes at 50°, producing α -chloronaphthalene and HCl . Naphthalene tetrachloride (1:2:3:4), formed finally, is a solid (m.p. 182°) which yields three isomeric dichloronaphthalenes, $\text{C}_{10}\text{H}_6\text{Cl}_2$, when heated with caustic potash. On

oxidation, it readily gives phthalic acid, showing the presence of all the chlorine atoms in one ring.

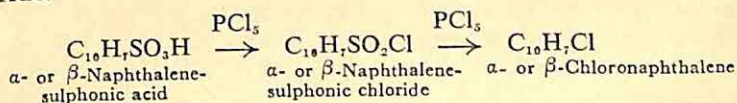
Halogen-substituted naphthalenes are prepared like halogenobenzenes. Nearly pure derivatives are obtained by chlorinating or brominating naphthalene at its boiling point or with iron catalyst above 80° —95% of α -derivative and 5% of β - are thus produced. With 1 mole of SO_2Cl_2 in presence of AlCl_3 at 25° , α -chloronaphthalene results.



The β -derivatives are prepared by indirect methods such as heating β -naphthol with PCl_5 or through diazo reaction from β -naphthylamine.



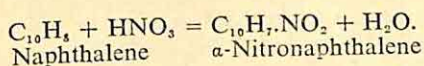
Both α - and β -chloro-derivatives can, however, be obtained by treating the corresponding naphthalenesulphonic acids with phosphorus pentachloride.



α -Chloronaphthalene is a colourless liquid (b.p. 263°) but the β -compound is a crystalline solid (m.p. 56°). The α -compound is sometimes used as a lubricant.

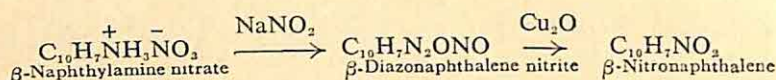
The halogen atoms in these derivatives are firmly linked to the nucleus as in halogen-substituted benzenes and are not removed by boiling alkalis. These are, however, somewhat more reactive. By exhaustive chlorination, all the H-atoms can be replaced by chlorine—per- or octa-chloronaphthalene, C_{10}Cl_8 , (m.p. 203°) is thus obtained. Polychloronaphthalenes, having good dielectric properties, are impregnating agents (*Halowax*).

Nitronaphthalenes.—Naphthalene readily yields nitro-derivatives when treated with a mixture of conc. nitric and sulphuric acids. α -Nitronaphthalene, $\text{C}_{10}\text{H}_7\text{NO}_2$, in 95% yield, is obtained by nitrating at 60° .

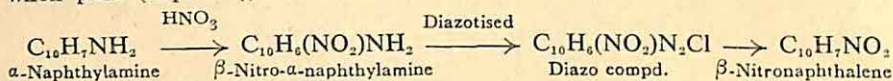


It is a yellow, crystalline solid (dimorphous, m.p. 52° and 58°), non-volatile in steam, insoluble in water but soluble in benzene, ether and hot alcohol. On further nitration at high temperature, it gives mainly 1:8-dinitronaphthalene. As the $-\text{NO}_2$ group deactivates the ring, the second $-\text{NO}_2$ group goes to the α -position in the second ring. Some 1:5-dinitronaphthalene is also formed. On oxidation, α -nitronaphthalene gives nitrophthalic acid, showing that the ring with the nitro group is more stable (p. 434). It yields α -chloronaphthalene with phosphorus pentachloride. It is used for making α -naphthylamine and also for removing fluorescence from mineral oils.

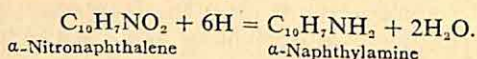
β -Nitronaphthalene, $\text{C}_{10}\text{H}_7\text{NO}_2$, cannot be prepared by direct nitration. It is obtained by treating β -naphthylamine nitrate with sodium nitrite and then with finely divided cuprous oxide. Naphthalene diazonium nitrite, first formed, decomposes to β -nitronaphthalene.



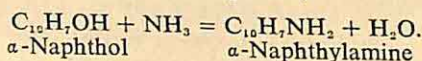
More conveniently, it is prepared by treating α -naphthylamine with dilute nitric acid. β -nitro- α -naphthylamine formed is treated with alcoholic hydrogen chloride in presence of finely powdered sodium nitrite. The amino group is thus diazotised, and finally removed by boiling. β -Nitronaphthalene is colourless when pure (m.p. 79°), and volatile in steam.



α - and β -naphthylamines or aminonaphthalenes, $\text{C}_{10}\text{H}_7\text{NH}_2$, resemble aniline in their behaviour, and are of considerable importance. Commercially, iron filings and HCl at about 50° reduce α -nitronaphthalene to α -naphthylamine. This is also formed when naphthalene is heated with sodamide, NaNH_2 .



α -Naphthol yields α -naphthylamine when heated to 250° with the molecular compound of ammonia and zinc chloride. The reaction is quicker than in the case of phenol (p. 385).



α -Naphthylamine forms colourless needles (m.p. 50°) which gradually turn brown on exposure to air. It sublimes readily, is volatile in steam, has a foul smell and is practically insoluble in water, but easily soluble in alcohol or benzene. It readily forms stable salts with mineral acids. The hydrochloride is slightly soluble in water, but is precipitated by HCl (contrast with aniline hydrochloride). Boiling chromic acid oxidises it to α -naphthaquinone, and permanganate to phthalic acid. α -Naphthylamine is converted into α -naphthol and 1:4-naphthylaminesulphonic acid which make azo dyes. It is also used in photography to obtain bluish tones.

An aqueous solution of a salt of α -naphthylamine (but not of the β -isomer) gives with ferric chloride (or other oxidising agents such as chromates) a blue precipitate. This is utilised for distinguishing them and also for the colorimetric estimation of chromates.

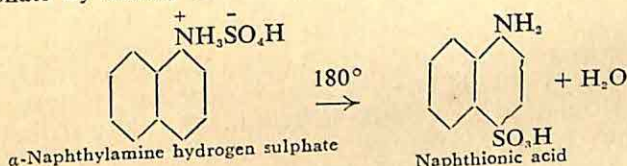
β -Naphthylamine may be obtained by reducing β -nitronaphthalene which, however, is difficult to prepare (p. 437). Technically, it is made, in high yield and purity, by heating β -naphthol with ammonia and zinc chloride at 250° , or with excess of aqueous ammonium sulphite or bisulphite at about 150° under pressure (*Bücherer reaction*). It forms colourless plates (m.p. 112°) which are odourless and volatile in steam. It is largely used for making azo dyes, and certain β -derivatives of naphthalene through diazotisation. Permanganate oxidises it to phthalic acid. α -Derivatives of naphthalene generally have lower m.p. than the β .

α - and β -sulphonic acids of naphthalene are formed when naphthalene reacts with conc. H_2SO_4 . The reaction is reversible, and

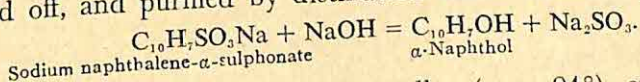
more energetic than with benzene. Below 80° , mostly the α -compound (m.p. 91°) is produced, while above 120° , the β -variety (m.p. 102°) predominates. The α - is largely converted into the β -form by conc. H_2SO_4 at about 180° . Superheated steam hydrolyses the α -acid into naphthalene and sulphuric acid, but not the β - which is thus obtained pure technically.

They are separated by forming calcium or lead salts, β -sulphonates being less soluble. The sulphonic acids are crystalline, hygroscopic solids closely resembling benzenesulphonic acid. They are highly soluble in water and yield naphthols on potash fusion, cyanides on distillation with pot. cyanide, etc. They are mostly converted into naphthols required for making dyes. The sulphonic acids and formaldehyde condense to synthetic tannins (*neradol ND*). On further sulphonation, the $-\text{SO}_3\text{H}$ group goes to the other ring (*cf.*, nitration of naphthalene); α -naphthalenesulphonic acid gives mainly 1:5-naphthalenedisulphonic acid with some of the 1:6-isomer. β -Naphthalenesulphonic acid forms chiefly 2:7-naphthalenedisulphonic acid and some of the 2:6-isomer.

Of the 14 isomeric naphthylaminesulphonic acids, $\text{C}_{10}\text{H}_6(\text{SO}_3\text{H})\text{NH}_2$, *naphthionic acid* (the 1:4-derivative) is the most important for making dyes such as Congo red. It is commonly prepared from α -naphthylamine hydrogen sulphate by baking at 180° (*cf.*, formation of sulphanilic acid, p. 357).



Naphthols or hydroxynaphthalenes are analogous to phenols and behave more or less similarly. Both α - and β -naphthols occur in small amounts in coal-tar. α -Naphthol, $\text{C}_{10}\text{H}_7\text{OH}$, is made by diazotising α -naphthylamine and boiling with water the product (*cf.*, formation of phenol from aniline, p. 382) or heating α -naphthylamine with dilute H_2SO_4 at 200° under pressure (contrast with aniline). It may also be obtained from β -benzylidenepropionic acid (p. 434), which proves the constitution of α -naphthol and eventually, that of naphthalene. α -Naphthol is, however, cheaply made from sodium naphthalene- α -sulphonate, $\text{C}_{10}\text{H}_7\text{SO}_3\text{Na}$, by alkali fusion at about 300° with a little water in iron vessel fitted with mechanical stirrers. The mass is poured into water and the sodium salt of α -naphthol formed is decomposed by carbon dioxide or dilute sulphuric acid. The crude α -naphthol is filtered off, and purified by distillation under reduced pressure.



α -Naphthol forms colourless needles (m.p. 94°), sparingly soluble in water, but readily soluble in ether, alcohol, and benzene. It has a faint phenolic smell, and resembles phenol. It is a disinfectant (and deodorant), being slightly more active than phenol. α -Naphthol is volatile at ordinary temperature. It dissolves in caustic alkalis (but not

in alkali carbonates), forming naphthoxides (e.g., $C_{10}H_7ONa$) which are decomposed by carbon dioxide. The phenolic H is replaceable by acyl or alkyl group, and the -OH by Cl or Br as usual. With ferric chloride it gives a violet precipitate of α -dinaphthol, $HOC_{10}H_6 \cdot C_{10}H_6OH$. α -Naphthol can be nitrated or sulphonated—the derivatives form dye intermediates. α -Naphthol ($k = 2.1 \times 10^{-10}$) is a slightly stronger acid than the β - ($k = 1.2 \times 10^{-10}$). The potassium salt of 2:4-dinitronaphthol-7-sulphonic acid is *naphthol yellow*; the sodium salt of 2:4-dinitronaphthol is *Martius' yellow*; these dye silk and wool. The -OH of α -naphthol is readily replaced by an $-NH_2$ group on heating with ammonia and zinc chloride (p. 438). α -Naphthol ethers are obtained by heating α -naphthol with an alcohol and H_2SO_4 , but *phenol ethers cannot be obtained similarly*.

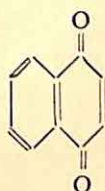
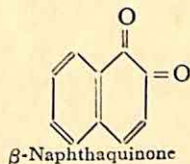
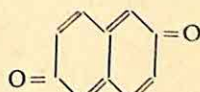
Tests for α -naphthol.—(i) A dilute alcoholic solution of α -naphthol gives with hot ferric chloride solution a violet ppt. of α -dinaphthol. (ii) A solution of α -naphthol forms with picric acid solution, both cold and saturated, orange crystals of picrate. (iii) On warming in dilute caustic soda solution with carbon tetrachloride and copper powder, it gives a blue colour (*distinction from β -naphthol which gives no coloration*).

β -Naphthol, $C_{10}H_7OH$, is made by alkali fusion of naphthalene- β -sulphonic acid like the α -compound. By diazo reaction, it may be obtained from β -naphthylamine which, however, is made from β -naphthol itself (p. 438). β -Naphthol forms lustrous, rhombic crystals (m.p. 123°) and closely resembles α -naphthol. It produces with ferric chloride a green coloration and afterwards a flocculent precipitate of β -dinaphthol, $HOC_{10}H_6 \cdot C_{10}H_6OH$. Unlike α -naphthol, it forms an insoluble calcium salt and is not volatile in steam. Both the naphthols, more commonly the β -isomer, are used in the dye industry. α -Naphthol couples with diazo-salts mainly in position 4 and to some extent in position 2 while β -naphthol does so only in position 1. β -Naphthol-sulphonic acids are more important for making various azo dyes, the SO_3H group has a solubilising effect.

β -Naphthol and its salicylic ester (*betol*) are good intestinal antiseptics. The β -naphthylethyl ether (*nerolin*) is a perfume for soaps. Some of the amidonaphthols are well-known photographic developers. α -Naphthol is a reagent in the Molisch test for proteins (p. 306). α -Nitroso- β -naphthol, $C_{10}H_6(NO)OH$, is a delicate reagent for the detection of cobalt; the corresponding nitro-compound, $C_{10}H_6(NO_2)OH$, which is more stable, is employed for estimating cobalt in presence of nickel.

Naphthaquinones, $C_{10}H_6O_2$, exist in three isomeric forms though six are theoretically possible; they may be obtained like benzoquinone. α -Naphthaquinone, the true analogue of *p*-benzoquinone, is prepared by oxidising naphthalene in acetic acid solution with chromic acid (benzene cannot be oxidised to quinone likewise), or with air in presence of vanadium pentoxide. α -Naphthylamine, 1:4-diamino- or dihydroxy-naphthalene and other α - or 1:4 derivatives of naphthalene produce α -naphthaquinone on oxidation. α -Naphthaquinone forms yellow plates (m.p. 125°). It has a pungent smell characteristic of quinones, sublimes at about 100° , and is volatile in steam. On reduction, it gives 1:4-dihydroxynaphthalene (*cf.*, properties of benzoquinone, p. 408). Vitamin K_1 and K_2 are α -naphthaquinone derivatives, which help coagu-

lation of blood. *Lawson*, 2-hydroxy- α -naphthaquinone, occurs in the leaves of Indian henna (*Lawsonia alba*); it dyes wool and silk an orange shade.

 α -Naphthaquinone β -Naphthaquinone

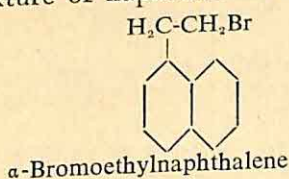
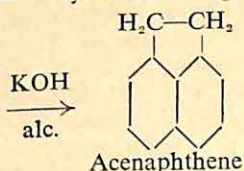
Amphi-naphthaquinone

β -Naphthaquinone is formed when α -amino- β -naphthol is oxidised with chromic acid or ferric chloride. Its red needles decompose at about 115° without melting; it is odourless and non-volatile. On reduction, it gives 1:2-dihydroxynaphthalene. Chlorine-water or hypochlorous acid opens up the quinone ring and gives phenylglyceric-*o*-carboxylic lactone. Both α - and β -naphthaquinone yield phthalic acid on oxidation, showing that the oxygen atoms are in the same ring. β -naphthaquinone behaves as an *o*-diketone.

Amphi-naphthaquinone has the oxygen atoms in different nuclei. It is prepared by oxidising 2:6-dihydroxynaphthalene in benzene with lead dioxide. It forms orange prisms (m.p. 135°), odourless and non-volatile. It is a stronger oxidising agent than its isomers.

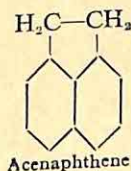
Corresponding to benzoic acid, there are the *naphthoic acids*, $C_{10}H_7COOH$, obtained by hydrolysing cyanonaphthalenes, and also by other methods for preparing aromatic acids (p. 410). Both α - and β -acid yield naphthalene on distillation with soda-lime. They form colourless needles, sparingly soluble in water; α -naphthoic acid melts at 160° and the β - at 182° .

Acenaphthene, $C_{12}H_{10}$, occurs in the heavy oil fraction of coal-tar and in petroleum tar. It may be made by treating α -bromo-ethyl-naphthalene with alcoholic potash, or by passing α -ethylnaphthalene, or a mixture of naphthalene and ethylene, through a red-hot tube.

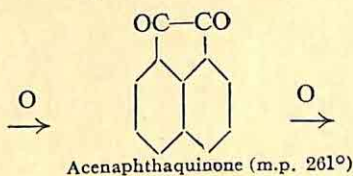
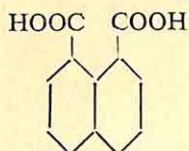
 α -Bromoethylnaphthalene

Acenaphthene

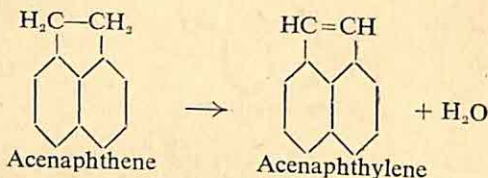
Acenaphthene forms colourless needles or leaflets (m.p. 95°), soluble in alcohol. With chromic acid, it yields a quinone and then naphthalic acid (1:8) which forms naphthalic anhydride on heating.



Acenaphthene

Acenaphthaquinone (m.p. 261°)Naphthalic acid (m. p. 266°)

Acenaphthene, therefore, contains the $-\text{CH}_2-$ groups in peri- or 1:8-position. Acenaphthaquinone, made technically from acenaphthene, is converted into some vat dyes. At red heat or with lead peroxide, acenaphthene loses hydrogen and forms acenaphthylene, a yellow solid (m.p. 93°).



QUESTIONS

1. What are naphthols? What is their commercial importance, and how are they prepared?
2. Make a comparative study of aniline and naphthylamine, and show that they are analogous compounds.
3. How are α -naphthol and β -naphthylamine prepared? Show that the formula commonly assigned to naphthalene is in agreement with its behaviour. B.Sc., London, 1924.
4. From what sources is naphthalene obtained? What products does it yield (a) on oxidation, (b) with H_2SO_4 , (c) with HNO_3 ? B.Sc., London, 1931.
5. How has the constitution of naphthalene been established? How would you obtain from naphthalene α - and β -naphthols, α - and β -naphthylamines, naphthionic acid, decahydronaphthalene, and 1:5-naphthaquinone? A.I.C., 1934.
6. Explain how naphthalene is used in the preparation of (a) β -naphthol, (b) β -nitronaphthalene, and (c) anthranilic acid. B.Sc., 1932, Punjab Uni.
7. Justify the structure assigned to naphthalene. B.A. & B.Sc., 1937, Bombay Uni.
8. How is naphthalene obtained on a large scale? Establish its constitution. B.Sc., Pass, 1951, Rajsthan Uni., B.A. & B.Sc., 1933, Allahabad Uni.
9. Describe how the structure of naphthalene has been established. B.Sc. Degree Exam. 1941, Annamalai Uni.
10. How is naphthalene manufactured? Describe how it is synthesised, and prove its constitution. What do you know about the isomerism of its derivatives? B.Sc., 1941, Agra Uni.
11. Indicate the method by which you will proceed to prepare any three of the following: (a) phthalic acid, (b) β -naphthol, (c) phenyl cyanide, (d) potato starch, and (e) acetone. B.Sc., 1942, Agra Uni.
12. You are given a mixture of acetone, phenol and naphthalene. How would you prepare pure specimens of the three components? Describe one method for identifying each of the substances. B.A. Degree Exam., 1942. Madras Uni.

CHAPTER XLIV

ANTHRACENE AND ITS DERIVATIVES

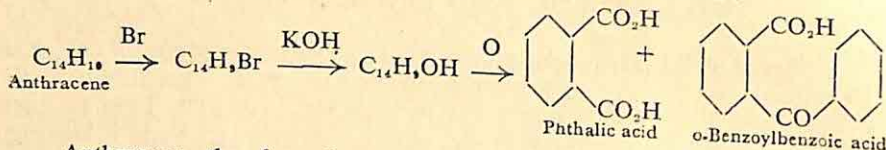
Anthracene, $C_{14}H_{10}$, a hydrocarbon of three condensed benzene nuclei, is important as the parent substance of many dyestuffs. Coal-tar, the chief source, contains 0.25-0.45% of it. In 1832 Dumas and Laurent isolated anthracene from coal-tar (*anthrax*, coal). During coal-tar distillation, it comes with phenanthrene, carbazole and other substances, between 270° - 360° , in *green oil* or *anthracene oil* (p. 318). On standing, a viscous mass separates, which is subjected to vacuum filtration; the crude anthracene cake (with about 20% anthracene) is agitated with light oil at 90° , the undissolved portion is filtered as before. The cake now contains about 35% of anthracene; it is heated to 100° and centrifuged to remove traces of oil. The product, '50% anthracene', is powdered and washed with solvent naphtha which dissolves phenanthrene, and then with pyridine which takes up carbazole. Anthracene is purified by sublimation.

Carbazole (m.p. 245°) may also be removed by distilling with pot. carbonate, non-volatile potassium carbazole, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix} \rangle NK$, is thus formed. The distillate containing anthracene and phenanthrene, is treated with carbon disulphide which dissolves phenanthrene.

Properties.—Pure anthracene forms colourless, glistening plates (m.p. 216° , b.p. 340°) with a blue fluorescence. It is insoluble in water, sparingly soluble in alcohol and ether, but readily soluble in hot benzene or toluene. Brilliant, ruby-red crystals of *anthracene picrate*, $C_{14}H_{10} \cdot C_6H_2(NO_2)_3OH$, (m.p. 138°) are obtained when *saturated* solutions of picric acid and anthracene (both in acetone or alcohol) are mixed together. This breaks up on adding a large volume of alcohol. Anthracene may be identified by its picrate.

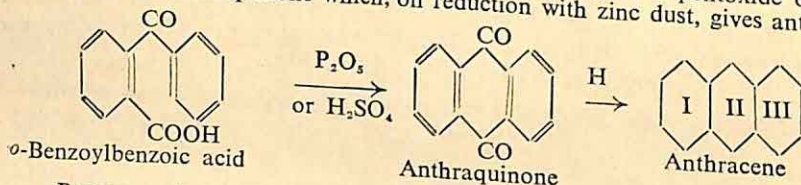
On oxidation, anthracene yields anthraquinone, more readily than naphthalene forms naphthaquinone, but under drastic conditions, phthalic acid is obtained. It is much easier to hydrogenate anthracene than benzene or naphthalene, e.g., with sodium amalgam in alcoholic solution, we get dihydroanthracene, $C_{14}H_{12}$. Halogens give both addition and substitution products of anthracene depending upon conditions. Thus at 0° anthracene 9,10-dibromide is obtained readily with bromine and 9,10-dibromoanthracene results with bromine in boiling carbon tetrachloride. Sulphuric acid readily produces anthracene-1- and -2- sulphonic acids. A saturated solution of anthracene in benzene or xylene, on exposure to sunlight, polymerises to *para-* or *di-anthracene*, $(C_{14}H_{10})_2$, a crystalline compound (m.p. 244°); 9 and 10 positions of one molecule link up with the corresponding positions of another. We get back anthracene on melting or keeping it in dark for a long time. Aqueous nitric acid oxidises anthracene to anthraquinone but in presence of acetic anhydride, 9- and 9:10-nitroanthracene may be obtained at 15° .

Constitution of anthracene.—From analysis, anthracene is $C_{14}H_{10}$; it behaves generally like benzene or naphthalene. With bromine, it forms bromoanthracene which, on potash fusion, gives a hydroxyanthracene. This, when oxidised, breaks up into phthalic acid and *o*-benzoylbenzoic acid:

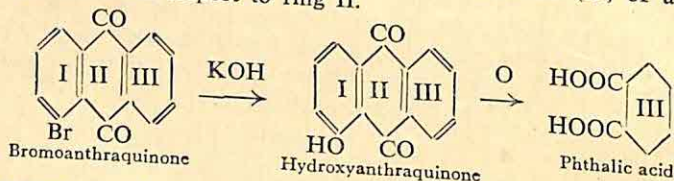


Anthracene, therefore, has at least two benzene rings; this also follows from the fact that anthracene, on oxidation, forms anthraquinone, $C_{14}H_8O_2$, which, on potash fusion at 250° , gives two molecules of benzoic acid. To explain these facts and provide for the normal valency of 14 C and 10 H atoms, anthracene has been given a three-fused-benzene-rings structure which has been confirmed by numerous syntheses.

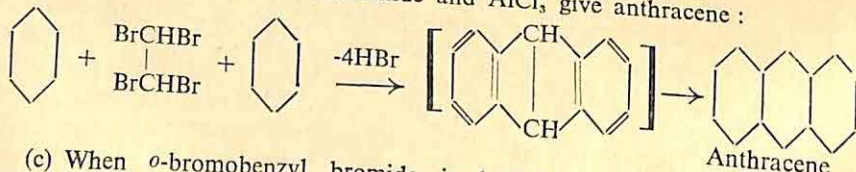
(a) *o*-Benzoylbenzoic acid (made from phthalic anhydride and benzene in presence of aluminium chloride), heated with phosphorus pentoxide or strong H_2SO_4 , forms anthraquinone which, on reduction with zinc dust, gives anthracene:



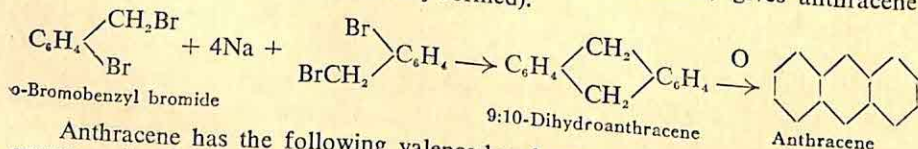
Because *o*-benzoylbenzoic acid has the $-COOH$ in *o*-position, ring II of anthracene must be in the *o*-position with respect to ring I. But if we start with *o*-benzoylbromobenzoic acid, we get bromoanthraquinone which, on alkali fusion, gives hydroxyanthraquinone. The latter, on oxidation, yields phthalic acid which must have resulted from the bromine-free ring of bromoanthraquinone (ring III). This also shows that ring III of bromoanthraquinone (ring III) is in the *o*-position with respect to ring II.



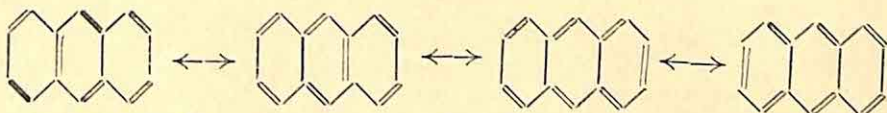
(b) Benzene, acetylene tetrabromide and $AlCl_3$ give anthracene:



(c) When *o*-bromobenzyl bromide is boiled in ethereal solution with sodium, we get dihydroanthracene which, on mild oxidation, gives anthracene (some phenanthrene is simultaneously formed).

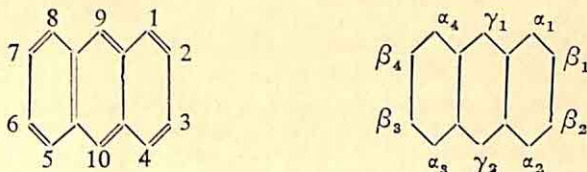


Anthracene has the following valence-bond structures; none, however, truly expresses its characteristics.



An average of these, a resonance hybrid, best explains its behaviour. X-ray measurements indicate that all the 14 C-atoms of anthracene are coplanar. The *para*-bond structure under (b) which accounts for the formation of anthracene from benzene and tetrabromoethane, and also the extraordinary reactivity of 9:10 positions, is untenable as the distance between the *para*-C-atoms in each ring is the same as in benzene, and also for other reasons.

Isomerism of anthracene derivatives.—For convenience of denoting the various substitution products of anthracene, the C-atoms linked with hydrogen are numbered or lettered as



The 1:2 bond has $\frac{3}{4}$ double bond character, and the 2:3 bond only $\frac{1}{4}$ (cf. naphthalene). It is clear that three isomeric monosubstituted anthracenes are possible *viz.*, α (1, 4, 5, 8), β (2, 3, 6, 7) and γ (9, 10) or *meso*. With similar substituents, we have 15 disubstituted anthracenes; with dissimilar, 23. The 9:10 positions are highly reactive; for instance, anthracene is readily oxidised to anthraquinone, reduced to 9:10-dihydroanthracene, and unites with two atoms of sodium in 9:10 positions. This is explained by the facts that unlike 1:2 or 2:3 addition product, a 9:10 additive product can have four valency-bond structures like anthracene; such structures, therefore, have higher resonance energy than 1:2 or 2:3 additive structures. An addition to the 9:10 carbon atoms leads to the formation of two isolated benzene rings and results in a molecule of great stability.

Derivatives of anthracene.— $\gamma\gamma$ -Dihydroanthracene, $C_{14}H_{12}$, a colourless, stable solid (m.p. 107°), is dehydrogenated to anthracene by heating with conc. H_2SO_4 . On catalytic hydrogenation at about 250° , anthracene successively forms tetra-, octa-, deca- and finally, perhydroanthracene, $C_{14}H_{24}$. Octahydroanthracene is the chief constituent of some synthetic lubricating oils. On passing chlorine into a cold solution of anthracene in carbon disulphide, $\gamma\gamma$ -anthracene dichloride,

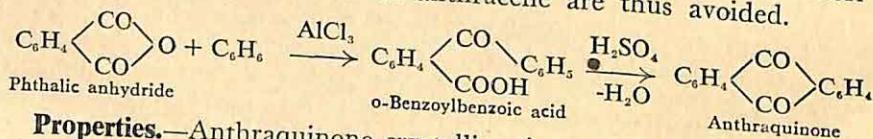
$C_6H_4 \begin{matrix} \text{CHCl} \\ \text{CHCl} \end{matrix} C_6H_4$, is obtained. This is unstable, and gives γ -monochloroanthracene, $C_{14}H_9Cl$, on warming or with caustic soda. Bromine behaves similarly. If, however, chlorine is passed into anthracene at 100° , substitution occurs, β -chloro- and $\gamma\gamma$ -dichloroanthracene are formed. Both are yellow, crystalline solids (m.p. 103° and 209° respectively), and both yield anthraquinone on oxidation. With oleum in acetic acid, anthracene forms α - and β -anthracene-sulphonic acids. Barium salt of the β -sulphonic acid only is insoluble in water; so they can be separated. On further sulphonation under

suitable conditions, six isomeric disulphonic acids result wherefrom various derivatives of anthracene are prepared. α - and β -hydroxy-anthracene are obtained by potash fusion of the corresponding sulphonophonic acids. They are known as α - and β -*anthrol* and behave like naphthols. γ -Hydroxyanthracene or *anthranol*, a yellow, unstable solid, (m.p. 120°), passes on, if heated rapidly, to the isomeric ketone, *anthrone*, a colourless, stable solid (m.p. 150°). Nitric acid oxidises anthracene to 9:10-anthraquinone; in acetic anhydride solution at 15°, 9-nitro- and 9:10-dinitroanthracene are obtained. These are stable and melt at 146° and 310° respectively.

Anthraquinone, $\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{smallmatrix} \text{C}_6\text{H}_4$, is readily obtained by oxidising anthracene with nitric or chromic acid. The other two isomers viz., 1:2- and 1:4-, are not important.

Preparation.—Finely powdered anthracene (10 g.) is dissolved in boiling glacial acetic acid (100 c.c.) in a flask with a reflux condenser. A mixture of chromic acid (20 g.), water (15 c.c.) and glacial acetic acid (75 c.c.) is run down drop by drop from a tap-funnel. The liquid is kept boiling for about 30 minutes, cooled and poured into a large volume of water (500 c.c.). Crude anthraquinone is filtered, washed with dilute warm caustic soda solution, and hot water several times. It is dried and purified by sublimation. It may be recrystallised from boiling acetic acid after decolorisation with animal charcoal.

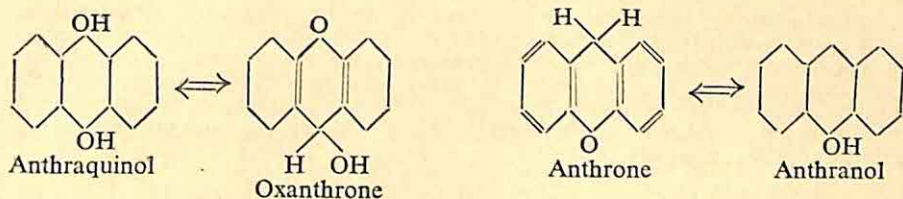
Anthraquinone, a dyestuff intermediate, is manufactured from sublimed anthracene with sodium dichromate and 50% sulphuric acid at about 100°. Oxidation of anthracene by air at about 400° in presence of V_2O_5 is cheaper. The cheapest industrial method is the condensation of phthalic anhydride with an excess of dry benzene in presence of aluminium chloride at 40°-50°. *o*-Benzoylbenzoic acid, first produced, is almost quantitatively transformed into anthraquinone by conc. H_2SO_4 at 150° (p. 444). Or in one step, by passing their mixed vapours over silica-alumina at 350-400°, we get anthraquinone. Laborious extraction and purification of anthracene are thus avoided.



Properties.—Anthraquinone crystallises in very pale yellow needles (m.p. 285°, b.p. 382°) which sublime at high temperature. It is insoluble in water, almost insoluble in alcohol but dissolves in glacial acetic acid, hot benzene, etc. It is a stable compound, not readily attacked by H_2SO_4 or HNO_3 . Anthraquinone, however, differs considerably from benzoquinone or naphthaquinone. It is not reduced by sulphur dioxide in water, it does not reduce ammon. silver nitrate nor does it liberate iodine from pot. iodide. It has no smell, and is not volatile in steam (cf., quinone, p. 407; naphthaquinone, p. 440). It, however, forms an oxime. Anthraquinone is not also an oxidising agent. It thus behaves more like a diketone than a *p*-quinone.

On warming with zinc dust and aqueous caustic soda, anthraquinone forms *anthraquinol* (labile) which tautomerises to *oxanthrone*.

On reducing anthraquinone with tin and hydrochloric acid in glacial acetic acid, we get *anthrone* which passes on to *anthranol*, its labile enol form, with alkali. Strong reducing agents (e.g., hydriodic acid at 150°) or distillation with zinc dust converts anthraquinone into anthracene.



Hydrogen peroxide is now made cheaply by catalytic hydrogenation of 2-ethylanthraquinone in an organic solvent to 2-ethylanthraquinol and oxidation of the latter with air back to the quinone (which is recycled) and hydrogen peroxide.

Tests for anthraquinone.—On heating 0.2 g. of finely powdered anthraquinone with about 5 c.c. of 10% caustic soda and a little zinc dust, an intense red colour of oxanthrone is produced. On shaking with air (when there is no zinc), the colour disappears, oxanthrone being oxidised to anthraquinone.

Alizarin, 1:2-dihydroxyanthraquinone, $C_{14}H_6O_2(OH)_2$, occurs, together with purpurin, as a glucoside in the root of madder (*Rubia tinctorum*) of which it is the chief colouring matter. Madder root has been extensively employed from the earliest times in India and Egypt, and in Europe from the 18th century, for dyeing Turkey Red. In Europe, the annual production of this dye was 150-180 million pounds. In 1827, Col and Robiquet obtained the dye as brilliant, red needles by heating madder root; they named it alizarin after *Alizari*, the Levantine term for madder.

Ruberythric acid, a glucoside of madder root, splits into alizarin and primeverose, a disaccharide of glucose and xylose, on enzymatic hydrolysis:

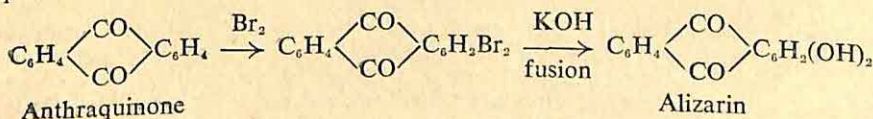


Madder was extensively cultivated in France. In 1869 alizarin was synthesised, and in less than ten years the cultivation of madder, which at that time fetched about £35,000,000 per year, was abandoned. It is the first natural dyestuff made in the laboratory.

Synthesis of alizarin.—In 1868 Graebe and Liebermann observed that alizarin, on heating with zinc dust, forms anthracene, a constituent of coal-tar.

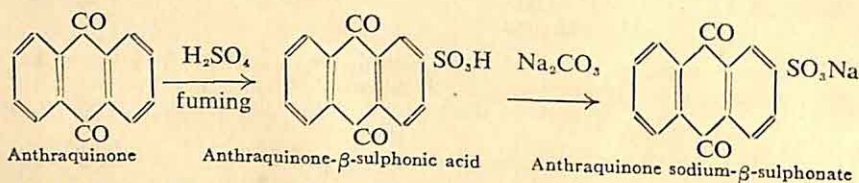


Alizarin was found to contain two oxygen atoms more than anthraquinone; its ready solubility in alkalis suggested their existence in the form of phenolic -OH group. In the following year, they succeeded in introducing the two -OH groups into anthraquinone, and luckily obtained alizarin—one of the ten possible dihydroxyanthraquinones. Anthraquinone was brominated to dibromo-anthraquinone directly, which, on potash fusion, gave alizarin:

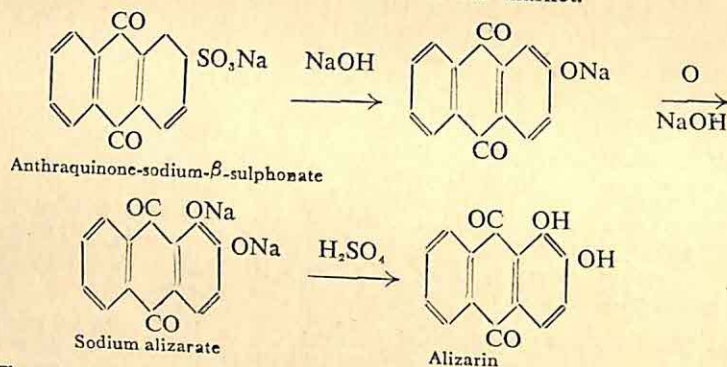


A cheaper method without bromine proved a commercial success. Caro, Graebe and Liebermann applied for English patent on June 25th 1869, and W. H. Perkin did the same next day—both parties worked out the process independently. By mutual agreement, Badische Anilin und Soda Fabrik manufactured the dye in Germany.

Manufacture of alizarin.—(i) Anthraquinone (made from anthracene) is heated with fuming H_2SO_4 (containing 40-50% of sulphur trioxide) at 160° in an iron vessel with mechanical stirrers. Practically all the anthraquinone is converted into its β -monosulphonic acid; because of the high temperature, little α -acid is formed (cf., α -sulphonic acid of naphthalene p. 438). This is dissolved in water and neutralised with sodium carbonate, when the sodium salt, being sparingly soluble, separates.



(ii) The crystalline sodium sulphonate is mixed with caustic soda and potassium chlorate, and heated in an autoclave to about 180° , when the $-\text{SO}_3\text{H}$ group is replaced by an $-\text{OH}$ and another $-\text{OH}$ is introduced into position 1. The fused, purple mass is acidified with dilute H_2SO_4 , alizarin separates as orange-yellow flakes. It is filtered in a filter-press and made into a paste with water containing about 20% alizarin for the market.



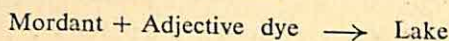
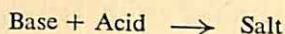
The yield of alizarin equals the weight of anthracene taken. The price of synthetic alizarin was 10s. a lb. in 1869 but only 1s. 4d. ten years later; this was 9d. per lb. less than the planter's cost of production.

Properties.—Alizarin crystallises in fine, ruby-red needles (m.p. 289°), soluble in alcohol and ether, but almost insoluble in water. It sublimes readily and is easily purified. As a phenol, it dissolves in caustic alkalis, forming a violet solution of alizarate. This with metallic salts forms insoluble metallic alizarates, known as *lakes*, having different colours. For example, aluminium alizarate is scarlet-red (*Turkey Red*), the ferric compound is dark violet, the calcium compound is blue, etc.

Alizarin has no affinity for cotton or other vegetable fibres. Cotton is, therefore, mordanted with various metallic hydroxides to have different shades. A fabric or yarn is dipped into a solution of aluminium acetate and heated in a current of steam, aluminium hydroxide deposits on the fibre. It is

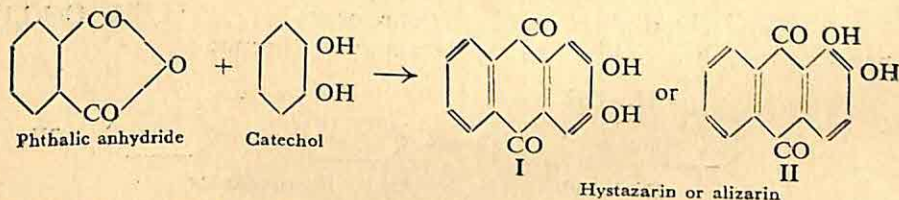
steeped in a suspension of alizarin in water, an insoluble red lake is formed on the fibre due to the combination of the faintly acidic alizarin with the feebly basic metallic oxide. The dye is thus permanently fixed on the yarn or fabric.

The word 'lake' was originally associated with 'lac' or 'lakh' (i.e., 1,00,000) which had reference to the very large number of lac insects (Indian lac). The term was next used for insoluble pigments derived from the insect. It now stands for any insoluble dyestuff that has no affinity for a fibre. These are called *adjective dyes* in contradistinction to direct or substantive dyes. Lakes are produced *in situ* on textile fibres. Their formation is apparently similar to that of salts:



For acidic dyes such as alizarin, the mordant is the base alumina or lime; for a basic dye, e.g., magenta, the suitable mordant is tannic acid.

Constitution of alizarin.—(i) Dibromo-anthraquinone, on potash fusion, yields alizarin, $\text{C}_{14}\text{H}_8\text{O}_4$. It is soluble in caustic alkalis, and gives anthracene, $\text{C}_{14}\text{H}_{10}$, on distillation with zinc dust. Alizarin is, therefore, a dihydroxy-anthraquinone. (ii) Alizarin is obtained (together with its isomer hystazarin) by heating phthalic anhydride and catechol in presence of H_2SO_4 (cf., formation of anthraquinone from phthalic anhydride and benzene, p. 446). As both must have the -OH groups in *o*-position, there are only two possibilities—alizarin is either I or II.



(iii) Now, alizarin forms two isomeric mononitro-derivatives, both having the -OH and -NO₂ groups in the same nucleus. This is possible if alizarin has the structure II inasmuch as I is capable of yielding only one. It is supported by the fact that each of the two monohydroxyanthraquinones, obtained by heating phthalic anhydride with phenol and H_2SO_4 , can be converted into alizarin. This would be impossible unless the -OH groups are in 1:2-positions as in II.

Here the quinonoid group, $\text{O}=\text{C}_6\text{H}_4=\text{O}$, is the chromophore and the -OH the auxochrome. Anthraquinone is a coloured substance—the chromogen—but not a dye as it has no auxochrome. *Alizarin orange* is nitro-alizarin; *alizarin blue* or *green* is a condensed pyridino-alizarin, and so on.

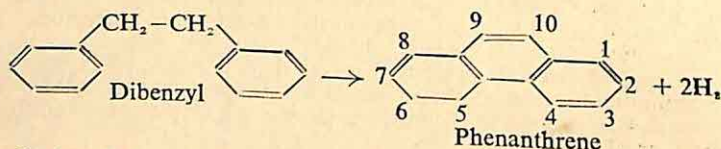
Purpurin, another glucoside of madder root, is the 1:2:4-trihydroxy-anthraquinone. It may be obtained by the oxidation of alizarin with manganese dioxide and sulphuric acid. Several other polyhydroxy-anthraquinones are important dyestuffs, forming lakes like alizarin.

Phenanthrene, $\text{C}_{14}\text{H}_{10}$, an isomer of anthracene, occurs with it in appreciable quantities in '50% anthracene', obtained from green oil. It is extracted therefrom with carbon disulphide or pyridine in which phenanthrene is more soluble. It may be separated from anthracene by preferential oxidation of the latter to anthraquinone with chromic acid. Phenanthrene forms white, glistening plates (m.p. 99° and b.p. 340°), with a blue fluorescence. It is insoluble in water, but dissolves

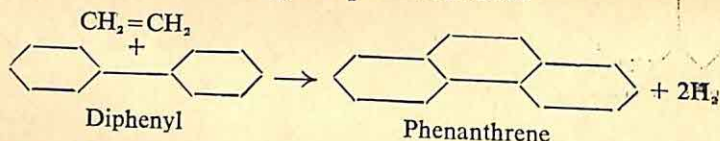
in ether, benzene, carbon disulphide, boiling alcohol, etc. It forms a golden yellow picrate (needles, m.p. 145°). Phenanthrene nucleus occurs in certain alkaloids (e.g., morphine), sex hormones, bile acids and sterols (e.g. cholesterol). Technically, it is unimportant; only a few dyes are derived from it.

On oxidation with chromic acid, phenanthrene forms phenanthraquinone, $C_{14}H_8O_2$; on further oxidation, we get diphenic acid, $C_{14}H_{10}O_4$, i.e., *diphenyldicarboxylic acid*, $HOOC-C_6H_4-C_6H_4-COOH$; it yields diphenyl, $C_6H_5-C_6H_5$, when distilled with soda-lime. Diphenic acid forms an anhydride, showing the proximity of the carboxyl groups. Phenanthrene is, therefore, a diphenyl derivative. Its structure follows from its syntheses:

(i) Dibenzyl with aluminium chloride in carbon disulphide yields phenanthrene:

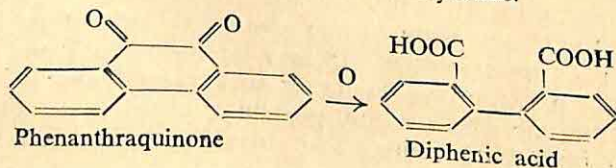


(ii) Similarly, diphenyl and ethylene, or stilbene, $C_6H_5CH=CHC_6H_5$, passed through a red-hot tube, gives phenanthrene:



Anthracene can be distinguished by its fluorescence in the visible part of the spectrum, phenanthrene shows none. From the intensity of the fluorescence bands, it can be estimated. 9,10 positions in phenanthrene are the most reactive, having a $4/5$ double-bond character (cf. anthracene, p. 445). Chlorine and bromine give unstable 9,10-dichloro- and 9,10-dibromo-derivatives while catalytic hydrogenation yields 9,10-dihydrophenanthrene.

Phenanthraquinone, $C_{14}H_8O_2$, obtained by oxidising phenanthrene with chromic acid in glacial acetic acid solution, forms odourless, orange needles (m.p. 207°) and is non-volatile in steam. It resembles closely β -naphthaquinone and behaves like a diketone, forming bisulphite derivatives, oximes, etc. Sulphur dioxide in water reduces phenanthraquinone to 9:10-dihydroxyphenanthrene or phenanthrahydroquinone. On oxidation with hydrogen peroxide in acetic acid, phenanthraquinone yields diphenic acid which gives diphenyl on distillation with soda-lime. Diphenic acid also forms an anhydride.



QUESTIONS

1. How is anthracene prepared? Give the important uses to which it is put, and discuss its constitution. B.Sc., 1934, Punjab Uni.
 2. How can anthracene and phenanthrene be synthetically obtained? How can you distinguish between the two?
 3. How has the structure of anthracene been established? B.Sc., 1937, Bombay Uni.
 4. Give the preparation and properties of alizarin and justify the structure assigned to it. B.A. & B.Sc., 1938, Bombay Uni.
 5. What is the principle involved in dyeing? What are lakes and mordants? Give examples.
 6. Describe the preparation of anthraquinone from commercial sources. How may it be synthesised, and what are its chief commercial uses? B.Sc., London, 1935.
 7. How is anthraquinone obtained from coal-tar? What synthetic methods are available for the preparation of this compound and its derivatives? Describe the preparation of a dyestuff from anthraquinone.
 8. How would you prepare alizarin in the laboratory? Derive its constitution. B.Sc. (Subs.) 1952, Bombay Uni.; B.Sc. Degree Exam. 1941, Madras Uni.
 9. Describe the relative properties of benzene, naphthalene and anthracene. B.Sc. (Principal Chemistry) 1942, Bombay Uni.
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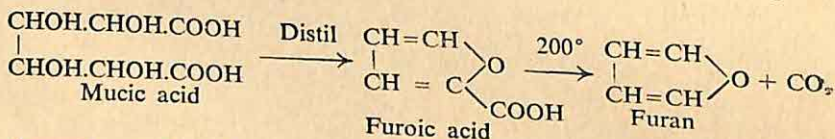
CHAPTER XLV

THE HETEROCYCLIC COMPOUNDS

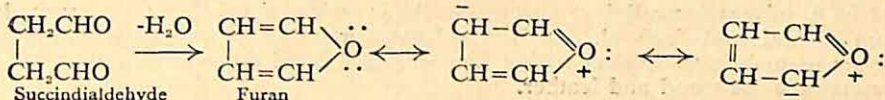
We have so far discussed mostly homocyclic compounds, *i.e.*, carbon rings. Compounds with other elements *e.g.*, oxygen, sulphur or nitrogen in the ring besides carbon, are called *heterocyclic* (Greek *heteros* other). Ethylene oxide (p. 110), the lactones (p. 189), succinimide (p. 245), glucose (p. 278), fructose (p. 280) and other cyclic sugars, phthalic anhydride (p. 420), uric acid (p. 298), etc., though 'heterocyclic', are relatively unstable and exhibit no aromatic behaviour. They are not true heterocyclic compounds which have five or six-membered rings, are quite stable and aromatic in character. They have conjugated double bonds. The chemistry of heterocyclic compounds is extensive and fairly complicated; chlorophyll, alkaloids, hæmoglobin, many plant pigments (*e.g.*, anthocyanins), numerous dyes (*e.g.*, quinoline dyes), etc. belong to this group. Some of the simplest members will be described here. Heterocyclics with nitrogen are the most numerous and important, then come those with oxygen; sulphur compounds are relatively few.

Five-membered rings.—The simplest are *furan*, C_4H_4O , *thiophene*, C_4H_4S , and *pyrrole*, C_4H_4NH . They are the building units of many natural products, and may be regarded as derived from benzene by the replacement of a $-CH=CH-$ with $-O-$, $-S-$ and $-NH-$ respectively. They closely resemble benzene.

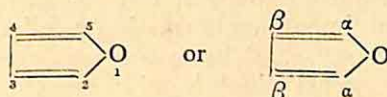
Furan, furfuran, C_4H_4O , occurs in pine wood-tar; it may be obtained by dry distilling mucic acid (p. 282); pyromucic or furoic acid, first formed, splits into furan and carbon dioxide. It is manufactured by passing furfural vapour and steam over zinc and manganese chromite at 400° .



Furan is a colourless liquid (b.p. 32°), very slightly soluble in water; it smells like chloroform. It may be nitrated with nitric acid in acetic anhydride (HNO_3 decomposes furan) to 2-nitrofuran. Substitution in furan proceeds more readily than in benzene. It is resinified by strong acids but is unaffected by alkalis. It cannot be halogenated or sulphonated directly. Passed over alumina at 450° , furan and ammonia form pyrrole; furan and sulphuretted hydrogen yield thiophene. The furan ring, like thiophene and pyrrole, is stable due to resonance; the carbon-oxygen distance (1.41 Å) is less than the normal value (1.43 Å) for a single bond. Furan is less aromatic than pyrrole which again is less so than thiophene; this corresponds to their resonance energy, 16, 22 and 29 k.cal./mole respectively. Its formation from succindialdehyde by dehydration with phosphorus pentoxide establishes its constitution:

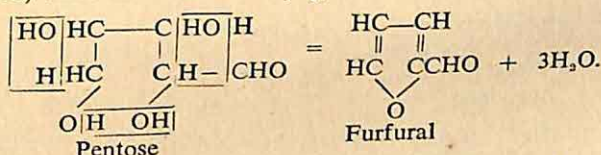


In the furan ring, the positions are denoted, starting from the hetero-atom, as follows; α -derivatives are more easily formed than β -.



A pine-wood splint, moistened with hydrochloric acid, turns green with furan. With isatin, it gives a violet colour. Furan itself has little use but some of its derivatives, e.g., furfural and tetrahydrofuran are technically important. Sodium and alcohol cannot reduce furan; hydrogen and Raney nickel at 80° give (in 90% yield) tetrahydrofuran, a useful solvent.

Furfural or furfuraldehyde, $\text{C}_4\text{H}_3\text{O}.\text{CHO}$, occurs in small amounts in clove oil and fusel oil; coumarone, a coal-tar constituent, is benzofuran. Furfural is formed, in definite but *not* quantitative yield, on distilling pentoses e.g., xylose, with 12% HCl. Substances containing pentosans, such as wood, bran, straw, jute, etc. and also pectin yield furfural (*furfur*, bran, *alium* oil) likewise. Pentoses are estimated by the amount of furfural they yield—one molecule of pentose (e.g., xylose or arabinose) should theoretically give one molecule of furfural.



Properties.—Freshly distilled furfural is a colourless, heavy, oily liquid (b.p. 162°) with a rather pleasant smell; it darkens on standing. It is fairly soluble in water, readily soluble in alcohol and volatile in steam. It resembles benzaldehyde and gives with aqueous caustic potash Cannizzaro reaction:



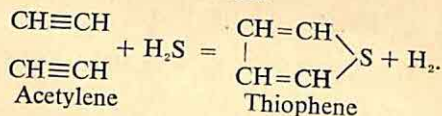
With ammonia, it forms *hydrofurfuramide*, $(\text{C}_4\text{H}_3\text{O}.\text{CH})_3\text{N}_2$, corresponding to hydrobenzamide (p. 403). With alcoholic pot. cyanide, it yields *furoin*, $\text{C}_4\text{H}_3\text{O}.\text{CHOH}.\text{CO}.\text{C}_4\text{H}_3\text{O}$ (cf., benzoin, p. 403) which may be oxidised to *furil*, $\text{C}_4\text{H}_3\text{O}.\text{CO}.\text{CO}.\text{C}_4\text{H}_3\text{O}$, analogous to benzil (p. 403). Furfural gives a pink colour with aniline acetate solution. Its condensation product with phloroglucinol or barbituric acid is utilised for its estimation. With zinc chromite at 400° , it gives furan and carbon monoxide. Dilute pot. permanganate oxidises furfural to furoic acid but sodium chlorate gives maleic anhydride, carbon dioxide and water, a reaction industrially followed. Hydrogen with $\text{CuO}.\text{Cr}_2\text{O}_3$ catalyst gives furfuryl alcohol but with nickel, tetrahydrofurfuryl alcohol results.

Furfural is commercially made from bran, oat hulls, corn cobs, etc., and dilute H_2SO_4 under pressure. Large amounts are used in Nylon production

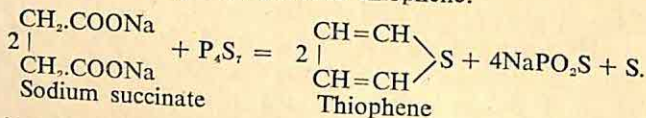
and as a solvent for cellulose esters. Synthetic resins of bakelite type are made from phenol and furfural. It is a solvent for cellulose esters, in synthetic rubber manufacture, in degumming kerosene and lubricating oils as well as a preservative for wood and leather.

Thiophene, C_4H_4S , the sulphur analogue of furan, occurs in coal-tar benzene (about 0.5%) and is detected by the indophenin reaction (p. 319). It was formerly believed to be a test for benzene. In 1883 V. Meyer, in a lecture experiment, embarrassingly failed to get the blue colour with synthetic benzene. The cause was traced to thiophene (*thio*, sulphur; *phene*, benzene) which he discovered in coal-tar benzene. Separation of thiophene (b.p. 84°) from benzene (b.p. 80.4°) is rather difficult. This is done by heating with mercury acetate—dimercurohydroxyacetate of thiophene, $HO.Hg.C_4H_4S.Hg.OOCCH_3$, precipitates—or by repeated treatment with conc. H_2SO_4 (p. 319), thiophene is more readily sulphonated than benzene. It is regenerated from the mercury compound by distilling with HCl , and from the thiophenesulphonic acid by superheated steam. Benzene is made thiophene-free easily by shaking with Raney nickel. Thiophene is more stable than furan or pyrrole. Biotin (vitamin H) contains thiophene nucleus. α -Terthienyl, a trimer of thiophene, occurs in the Indian marigold plant.

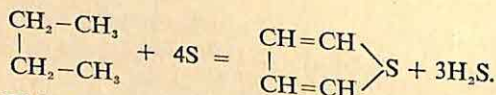
Synthesis.—(i) By passing acetylene and hydrogen sulphide over alumina at 400° , or acetylene alone over iron pyrites at about 300° ; some of the homologues of thiophene are also formed.



(ii) Sodium succinate and phosphorus heptasulphide, P_4S_7 , (formerly called trisulphide) when heated together, produce thiophene:



(iii) It is now manufactured by passing *n*-butane and sulphur vapour, both preheated to 600° separately, into a reaction tube at 650° for a contact time of .07 second, the exit gases are cooled rapidly. The unreacted materials are recycled.

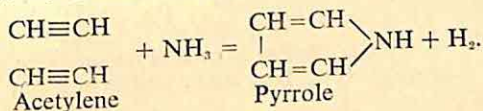


Properties.—Thiophene is a colourless, mobile liquid with a faint odour of benzene. It is heavier than water with which it is immiscible. It resembles benzene but is sulphonated more readily *e.g.*, at room temperature; Cl_2 or Br_2 easily replaces H in position 2 and 5. It is very difficult to reduce thiophene. Its homologues may be obtained by Wurtz-Fittig reaction; these yield thiophene carboxylic acids on oxidation. Thiophene can be nitrated by passing its vapour into fuming nitric acid, but not in the ordinary way. Like furan, it is stabilised by resonance, the normal carbon-sulphur bond distance of 1.81 Å is reduced

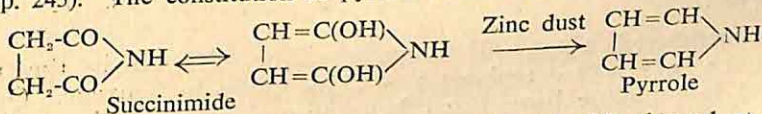
to 1.74 Å. Some drugs, dyes and resins are made from thiophene. Tetrahydrothiophene has a strong odour of coal gas; it is added to natural gas for detecting leakage in town gas supply.

Pyrrole, C_4H_4NH .—Chlorophyll, nicotine, cocaine, atropine, indigo, hæmatin (the red pigment of blood), etc., are derivatives of pyrrole, the nitrogen analogue of furan. It occurs in small quantities in coal-tar, and in fairly large amounts in bone oil (or Dippel's oil) produced by the dry distillation of bone-meal. Bone oil is fractionated, the portion coming between 100° – 150° contains pyrrole. Pyridine bases are removed from this fraction by washing with dilute H_2SO_4 and the nitriles of fatty acids by hydrolysis with boiling caustic potash solution. The liquid is dehydrated, and boiled with *solid* caustic potash; potassio-pyrrole, C_4H_4NK , separates as a solid. This is washed with ether and decomposed by water to pyrrole which is finally purified by distillation. It is of little commercial importance. It dissolves cellulose acetate and caffeine.

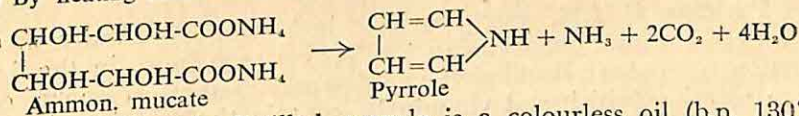
Synthesis.—(i) By passing acetylene and ammonia through a red-hot tube :



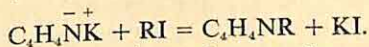
(ii) From succinimide on electrolytic reduction or distillation with zinc dust (p. 245). The constitution of pyrrole follows from this synthesis.



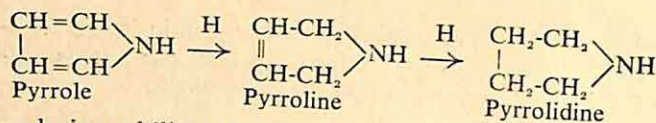
(iii) By heating ammonium mucate (or saccharate) with glycerol at 200° :



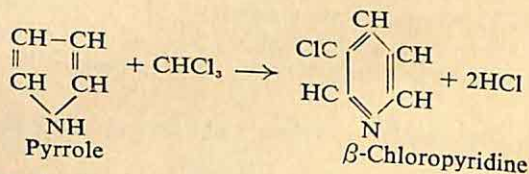
Properties.—Freshly distilled pyrrole is a colourless oil (b.p. 130° , sp. gr. 0.948 at 20°), smelling like chloroform; it is little soluble in water but readily soluble in alcohol and ether. It turns brown in air and slowly forms a resinous mass (*cf.* pyridine). Pyrrole behaves as a very weak acid and base. Thus, it slowly dissolves in cold, *dilute* mineral acids, and also reacts with metallic potassium in petroleum ether, or with solid KOH on heating, evolving hydrogen and forming potassium pyrrole. It is, however, insoluble in aqueous alkalis. The metallic derivatives are hydrolysed by water. Potassio-pyrrole readily reacts with alkyl or aryl iodides, the derivatives are tertiary bases :



As a secondary amine, pyrrole gives a nitrosoamine and an acetyl derivative. On reduction with zinc dust and acetic acid, we get pyrrolidine (b.p. 91°). This, on further reduction with red phosphorus and hydriodic acid, or nickel and hydrogen at 200° , yields pyrrolidine (b.p. 88°); both are strong bases.



Pyrrole is stabilised by resonance (resonance energy 24 k cal. per mole) as thiophene or furan. Like an aromatic compound, it forms substitution products but it cannot be nitrated or sulphonated, strong acids causing resinification; H_2SO_4 or HNO_3 destroys the pyrrole ring. It couples with diazo-salts and readily forms halogen substitution products in non-acidic medium. With strong acids, pyrrole probably polymerises to solid *pyrrole red*. On heating with chloroform and sodium ethoxide, in absence of water, β -chloropyridine results.



Iodine and pyrrole in dilute alcoholic caustic soda, give tetraiodopyrrole or *iodol*, $\text{C}_4\text{I}_4\text{NH}$, an odourless (but less toxic) substitute for iodoform as a surgical dusting powder.

Test.—Pine-wood shavings, moistened with HCl , turn crimson-red in vapour of pyrrole or its derivatives (*pyrros* fiery red, *oleum* oil). The picrate melts at 69° .

Six-membered rings.—Of these, pyridine, $\text{C}_5\text{H}_5\text{N}$, is the most important; here $-\text{N}=\text{CH}-$ replaces a $-\text{CH}=\text{CH}-$ group in benzene. Quino-alkaloids contain these nuclei.

Pyridine, $\text{C}_5\text{H}_5\text{N}$, was discovered in bone oil by Anderson (1851). It occurs in small quantities in Californian petroleum, in the light oil fraction of coal-tar distillation (p. 318) and in tobacco smoke, coming from nicotine (which and vitamin B_6 contain the pyridine ring). The light oil is agitated with dilute sulphuric acid in a lead-lined vessel, pyridine and other bases form a dark-coloured aqueous layer as sulphates. This is isolated, and treated with an excess of moderately conc. caustic soda, the free bases separate as a dark-brown oil. Pyridine is obtained by fractional distillation. Coal-tar, the chief commercial source, contains about 0.1% of pyridine.

Properties.—Pyridine is a colourless, mobile, hygroscopic liquid (b.p. 115° , sp. gr. 1.003 at 0°) with a disagreeable smell. It is miscible with water, alcohol, and ether in all proportions; from solution it can be salted out. Pyridine is a weak, tertiary base ($k = 2.3 \times 10^{-9}$), much weaker than ammonia but slightly stronger than aniline or pyrrole; it is alkaline to litmus. It readily forms quaternary compounds with alkyl iodides; methylpyridinium iodide, $\text{C}_5\text{H}_5\text{N}^+(\text{CH}_3)\text{I}^-$, is a crystalline solid. These yield strongly basic, quaternary hydroxides with moist silver oxide. Pyridine cannot be acetylated; it does not react with nitrous acid nor responds to the carbylamine reaction (cf., tertiary amines,

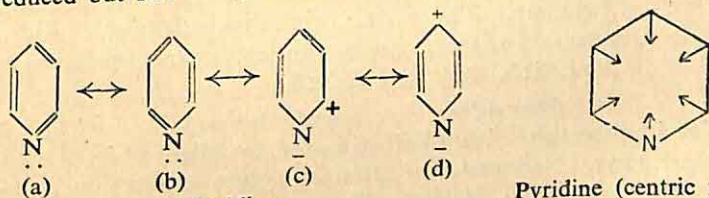
p. 207). It readily forms salts with acids *e.g.*, $C_5H_5^+NHCl^-$; these are mostly soluble in water except the ferrocyanide and the perchlorate. Crude pyridine may be purified by forming the ferrocyanide. Pyridine forms an orange-yellow, crystalline and sparingly soluble double-salt with platinic chloride, $(C_5H_5N.HCl)_2PtCl_4$ (m.p. 240°) and a picrate (m.p. 167°) with picric acid.

Pyridine is more stable than benzene (resonance energy 43 k cal. per mole, *i.e.*, 5 k cal. more than benzene); it is almost indifferent to boiling HNO_3 , chromic acid, $KMnO_4$, etc. It shows aromatic characters—it is slowly sulphonated to β -pyridinesulphonic acid with conc. H_2SO_4 at 350° and nitrated to β -nitropyridine with KNO_3 and fuming H_2SO_4 at 300° . Halogen-substituted products may be obtained with difficulty, *e.g.*, at about 400° in vapour phase. Alkylpyridines are readily oxidised to pyridine-carboxylic acids. α -Aminopyridine, $C_5H_4(NH_2)N$, obtained by heating pyridine with sodamide, $NaNH_2$, in toluene solution, can be diazotised like aniline. Catalytic or electrolytic reduction, or sodium and boiling ethanol, readily convert pyridine to hexahydropyridine or piperidine, $C_5H_{11}N$. Conc. H_2SO_4 at 300° oxidises piperidine back to pyridine. Conc. HI at 300° splits it into *n*-pentane and ammonia:

$$C_5H_5N + 10H = C_5H_{11} + NH_3.$$

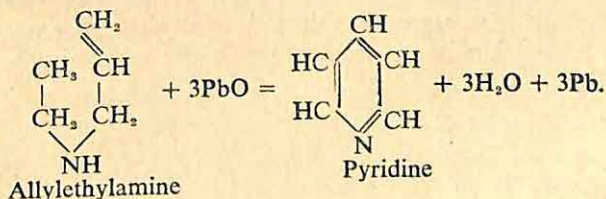
Constitution.—(i) The molecular formula of pyridine is C_5H_5N ; it is aromatic and closely resembles benzene. (ii) It is a tertiary base, forming methylpyridinium iodide with CH_3I . It does not react with HNO_3 nor gives carbylamine reaction.

Based on these facts, Körner (1869) put forth a ring structure for pyridine, similar to the Kekulé structure for benzene, which has been confirmed by synthesis. A centric formula like that of benzene (p. 323) was also suggested. Pyridine is a resonance hybrid; the lone pair of electrons in nitrogen is free and combines with a proton readily. This explains why pyridine is more readily reduced but less easily oxidised than benzene.

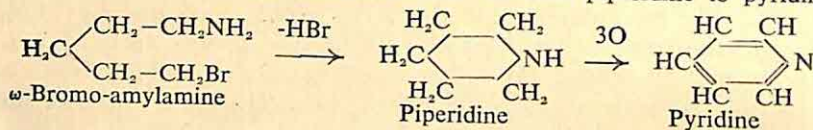


The polar structures (c) and (d) are supported by its high dipole moment and somewhat longer C—N bond length (1.37 Å in place of 1.33 Å for a half double bond as in benzene).

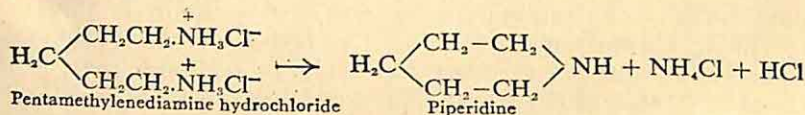
Synthesis of pyridine.—(a) Allylethylamine forms pyridine when passed over heated litharge, PbO :



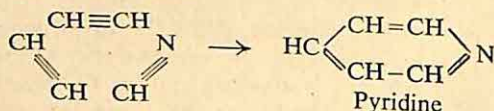
(b) Normal ω -bromo-amylamine gives piperidine on heating with alkali; strong H_2SO_4 at 300° or nitrobenzene at 260° oxidises piperidine to pyridine:



Piperidine is also obtained from pentamethylenediamine hydrochloride by dry distillation:

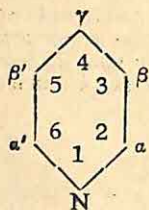


(c) By passing hydrocyanic acid vapour and acetylene through a red-hot tube, pyridine is formed in low yield.



Uses.—Pyridine, an important solvent, has also sufficient demand for denaturing alcohol. It is sometimes used for exterminating plant pests. Sulphapyridine is an effective sulpha drug. Pyridine is a catalyst in reactions involving the elimination of acids (e.g., acetylation).

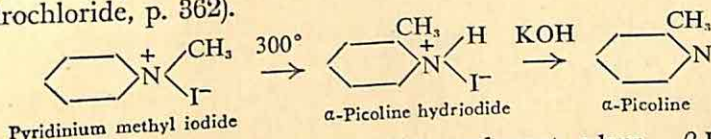
Isomerism of pyridine derivatives.—The structure of pyridine demands that there should be three isomeric monosubstituted pyridines; all are known. The positions α and α' are identical as also β and β' with respect to the nitrogen but the γ -position is different from both. α -, β - and γ -positions in pyridine correspond to ortho-, meta- and para-positions respectively of benzene. There are six disubstitution products, if the substituents are similar, corresponding to 2:3, 2:4, 2:5, 2:6, 3:4 & 3:5.



Piperidine or hexahydropyridine, $\text{C}_5\text{H}_{11}\text{N}$, was first obtained by heating with alkali *piperine*, an alkaloid in black pepper whence the name. Reduction of pyridine gives piperidine (p. 457). It may also be obtained from ω -bromo-amylamine. The structure of piperidine follows from these syntheses. Piperidine is a colourless liquid (b.p. 106°) with a pungent odour of pepper, miscible with water, alcohol, benzene, and ether. It has no aromatic properties and is oxidised to pyridine by nitrobenzene, or conc. H_2SO_4 at 300° . It is a strong, secondary base ($k_b = 1.6 \times 10^{-3}$) much stronger than pyridine. It is forming an acetyl and a nitroso-derivative and absorbing carbon dioxide from the air. Its aqueous solution precipitates heavy metals as hydroxides. Piperidine is an accelerator in the vulcanisation of rubber.

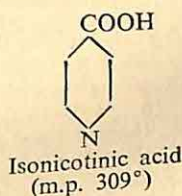
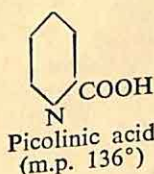
Alkylpyridines resemble the parent substance and occur with it in coal tar and bone oil. They are separated from pyridine by fractional distillation, or fractional crystallisation of their salts. The three isomeric methylpyridines are known as *picolines*, the six dimethylpyridines as

lutidines and the six trimethylpyridines as *collidines*. Lutidines are isomeric with toluidines. On oxidation, alkylpyridines yield the corresponding pyridine-carboxylic acids, having as many -COOH groups as there are side-chains. Friedel-Crafts alkylation of pyridine is not practicable as aluminium chloride combines with the N atom giving it a positive charge. α -Alkylpyridines result on heating quaternary pyridinium compounds (cf., formation of toluidine from methylaniline hydrochloride, p. 362).

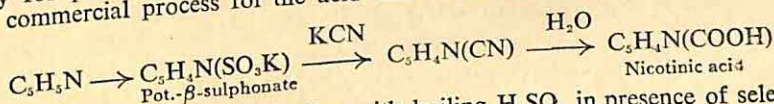


Methylpyridines are all liquids with unpleasant odour. β -Picoline (b.p. 142°) is formed when strychnine is heated with lime. α -Picoline (b.p. 129°) is soluble in water. It is an insecticide and an accelerator in the vulcanisation of rubber.

Pyridine-carboxylic acids.—Three monocarboxylic acids of pyridine, obtained by oxidising the corresponding alkylpyridines, are crystalline solids, soluble in water. They form salts with acids as well as bases (cf., glycine, p. 183).

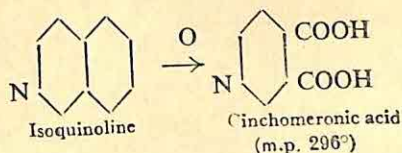
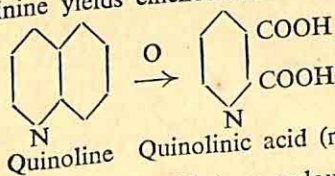


Pyridine- α -carboxylic acid readily loses carbon dioxide on heating, and produces an orange colour with ferrous sulphate. Picolinic acid can thus be distinguished from the other two. Nicotinic acid or *niacin* is obtained from the alkaloid *nicotine*, and picolinic acid from coniine, by oxidation. Nicotinic acid, also called vitamin P.P. (pellagra-preventing), is one of the components of vitamin B complex; it occurs in meat, liver, rice polishings and yeast. It is a remedy for pellagra (*pelle agra* rough skin), a disease resembling leprosy. A cheap commercial process for the acid starts from pyridine:



It is also made by oxidising quinoline with boiling H_2SO_4 in presence of selenium dioxide.

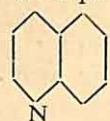
Of the pyridine dicarboxylic acids, *quinolinic* and *cinchomeronic* acids are the most notable. They are obtained by the oxidation of quinoline and isoquinoline respectively with pot. permanganate. Oxidised with nitric acid, quinoline yields cinchomeronic acid.



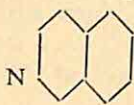
Quinolinic acid is a colourless solid, slightly soluble in water; it loses carbon dioxide, when heated, forming nicotinic acid. With ferrous sulphate, it gives an orange colour like picolinic acid. Cinchomeronic acid, on heating,

yields nicotinic and isonicotinic acid. Both form anhydrides on heating with acetic anhydride (cf., phthalic acid, p. 419), and pyridine on distillation with lime.

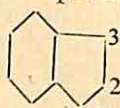
Condensed ring systems.—Of the condensed, heterocyclic systems, quinoline, isoquinoline and indole are important.



Quinoline



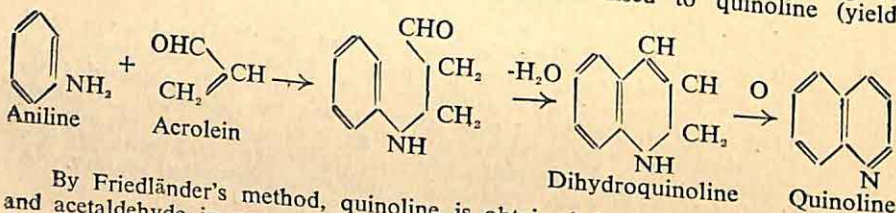
Isoquinoline



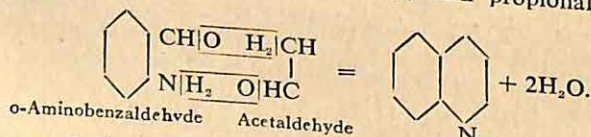
Indole

Quinoline, C_9H_7N , occurs, with isoquinoline, in coal-tar and bone-oil. It is rather difficult to separate them in pure state due to their close b.p. Some petroleum distillates contain quinoline and alkyl quinoline. Quinoline was obtained by Gerhardt in 1842 by distilling quinine with caustic potash. The source and its oily nature account for its name *quinoline*, originally *quin olein*. Quinoline and its derivatives are conveniently made by *Skraup synthesis*.

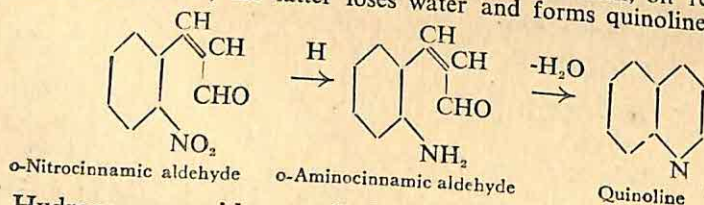
This consists in heating together a mixture of aniline, glycerol, conc. H_2SO_4 and a mild oxidising agent such as nitrobenzene or arsenic acid. Boric acid or ferrous sulphate moderates the reaction which is exothermic and may be violent. After the reaction is over, the mixture is made alkaline with caustic soda and steam distilled. Quinoline and unchanged aniline pass over; they are separated by fractional distillation. The mechanism of the reaction is believed to be as follows: (i) Glycerine is dehydrated to acrolein by conc. H_2SO_4 (p. 114). (ii) Aniline forms with acrolein an intermediate addition product, β -arylamino aldehyde. (iii) This, on ring closure by dehydration, gives 1:2-dihydroquinoline. (iv) The latter is finally oxidised to quinoline (yield about 90%).



By Friedländer's method, quinoline is obtained from *o*-aminobenzaldehyde and acetaldehyde in presence of dilute alkali; with propionaldehyde, 3-methylquinoline results.

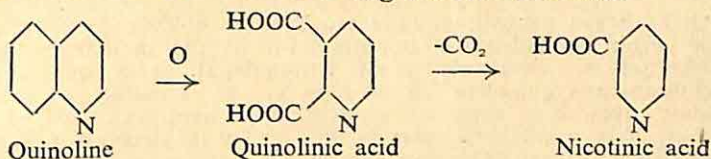


Baeyer made it from *o*-nitrocinnamic aldehyde which, on reduction, gives the amino-compound; the latter loses water and forms quinoline.

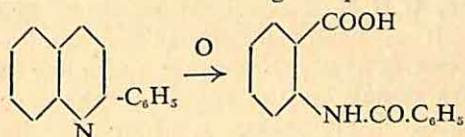


Hydrogen peroxide or alkaline pot. permanganate oxidises it to oxalic and quinolinic acid (cf., formation of phthalic acid from

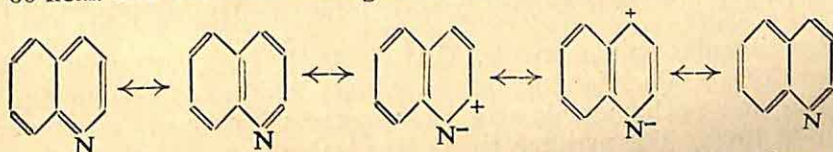
naphthalene, p. 419) which on heating gives nicotinic acid. The pyridine ring is more stable than the benzene ring towards oxidants.



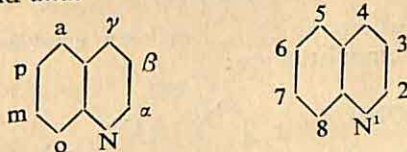
Pot. permanganate oxidises 2-phenyl-quinoline to benzoyl-anthranilic acid, the presence of a benzene ring in quinoline is thus proved:



Quinolinic acid has the -COOH group in *o*-position, so the benzene and pyridine rings are also fused in *o*-positions. The resonance energy is 69 kcal. and the contributing forms are



The isomeric derivatives are many as no two positions are identical with respect to nitrogen. The positions in pyridine nucleus are denoted by α , β and γ , while those in the benzene ring by *ortho*, *meta*, *para* and *ana*.



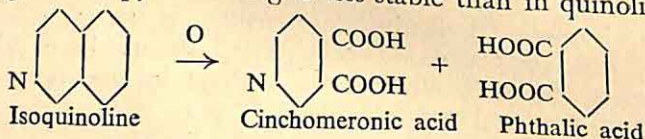
Properties.—Quinoline is a colourless, oily liquid (b.p. 237°), miscible with alcohol, ether, etc., but almost insoluble in water (cf. pyridine). It has a sharp smell like pyridine. It is a weak ($K_b = 3.2 \times 10^{-10}$) tertiary base, and readily forms, with mineral acids, crystalline salts such as quinoline hydrochloride, $C_9H_7N.HCl$. These with K_2CrO_4 , produce insoluble quinoline chromate, $(C_9H_7N)_2H_2CrO_4$, which serves as a test for the base. With CH_3I , quinoline forms methyl quinolonium iodide, $C_9H_7N^+(CH_3)I^-$, a crystalline solid (m.p. 133°). Nitration and sulphonation occur in the benzene ring; fuming HNO_3 gives 5- and 8-nitroquinoline. On catalytic hydrogenation, or with tin and HCl , hydrogen goes first to the pyridine ring, 1:2:3:4-tetrahydroquinoline being formed. The benzene ring is attacked next, decahydroquinoline is thus produced. If in Skraup's synthesis, aniline is replaced by substituted aniline, say, toluidine, substituted quinoline results, the substitution being in the benzene ring. Again, if *o*-aminobenzaldehyde is condensed with a ketone containing $-CH_2-CO-$ group,

substituted quinolines are formed, the substitution being in the pyridine ring.

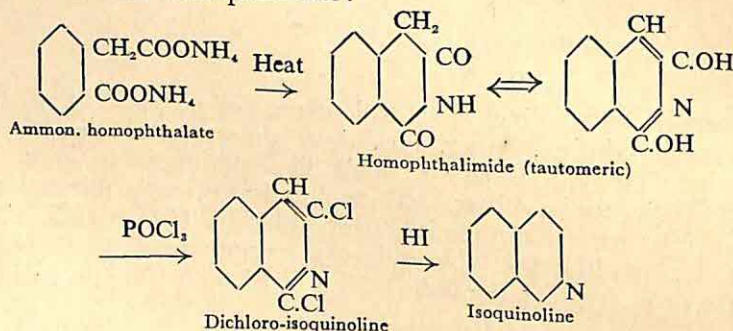
All the seven methylquinolines are known. *a*-Methylquinoline or *quinaldine* (which occurs in coal-tar) is important for its use in making the costly dye *quinoline yellow*. *Plasmoquine*, an anti-malarial, is a quinoline derivative. Iodochlorohydroxyquinoline or *vioform* is an effective amebicide. Some quinoline dyes are excellent photographic sensitizers. 8-Hydroxyquinoline (made by Skraup synthesis using *o*-aminophenol in place of aniline) precipitates quantitatively Cu and Zn from very dilute solution of their salts by forming chelate compounds and is used for their estimation. Quinoline is an important solvent.

Isoquinoline, C_9H_7N , has a benzene ring fused to a pyridine ring in β,γ -position. It invariably accompanies quinoline from coal-tar and forms only about 1% of the crude quinoline fraction. They are separated by fractional crystallisation of their sulphates from ethyl alcohol in which isoquinoline sulphate is insoluble. Morphine, narcotine, papavarine, etc., have isoquinoline nucleus. Isoquinoline smells like quinoline which it resembles closely. It melts at 24° and boils at 243° . Isoquinoline is a slightly stronger base than quinoline ($k_b = 1.1 \times 10^{-9}$). As a tertiary base, it forms quaternary alkyl iodides.

Methyl isoquinolonium iodide, $C_9H_7N^+(CH_3)I^-$, is a crystalline solid (m.p. 159°). Alkaline pot. permanganate oxidises isoquinoline to phthalic and cinchomeronic acid, showing the presence of benzene and pyridine rings. The pyridine ring is less stable than in quinoline.



The structure of isoquinoline has been established by its synthesis from ammonium homophthalate:

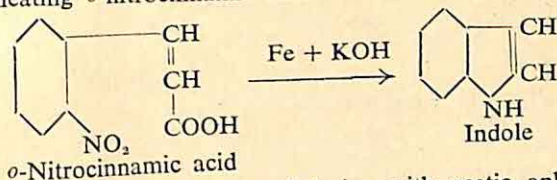


Homo- and nor- indicate higher and lower homologues respectively.

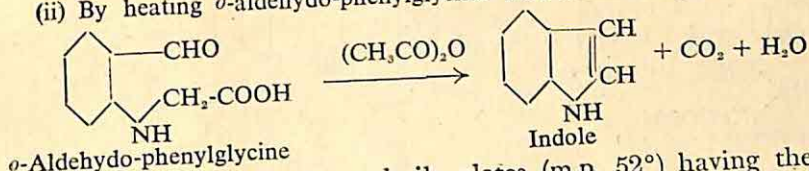
Indole or benzopyrrole, C_8H_7N , has a benzene nucleus fused with a pyrrole ring. It is the parent substance of indigo and occurs in the oil of *jasmine* (about 2.5%), in *neroli oil* and the heavy oil of coal-tar distillation. Indole is formed when some proteins putrefy or are decomposed by pancreatic fermentation; hence its occurrence in human faeces. *Tryptophan*, an essential amino-acid, is an indole derivative. Bayer (1868) first obtained indole by distilling indigo with zinc dust.

The name is derived from this fact. Indole-3-acetic acid, a plant growth hormone, occurs in human urine and higher plants. Indole may be prepared:

(i) By heating *o*-nitrocinnamic acid with caustic potash and iron filings:



(ii) By heating *o*-aldehydo-phenylglycine with acetic anhydride:

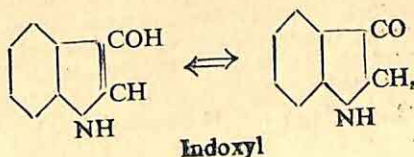
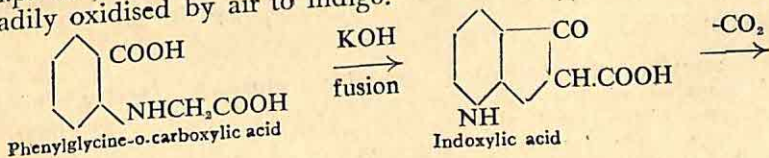


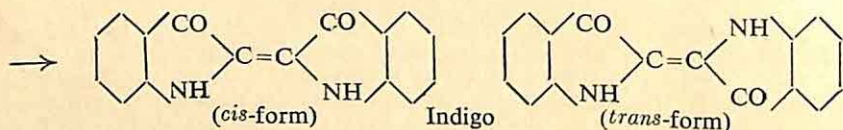
Indole forms colourless volatile plates (m.p. 52°) having the smell of faeces, if not quite pure. After thorough purification and high dilution, it has a flowery odour and is used in perfumes, and for stimulating the odour of flowers. It is oxidised by ozone to indigo. Indole imparts a cherry-red colour to pine-wood shavings moistened with alcohol and HCl. It is volatile in steam. Indole resembles pyrrole and forms a sodium and a potassium salt. Substituents, however, more readily go to the β -position which is activated by the benzene ring. It is a very weak, secondary base, and forms an acetyl derivative. It gives a bright red, crystalline picrate by which it is identified.

Skatole, β -methylindole, $\text{C}_8\text{H}_7\text{CH}_3$, occurs in civet and faeces, and is responsible for their repugnant odour.

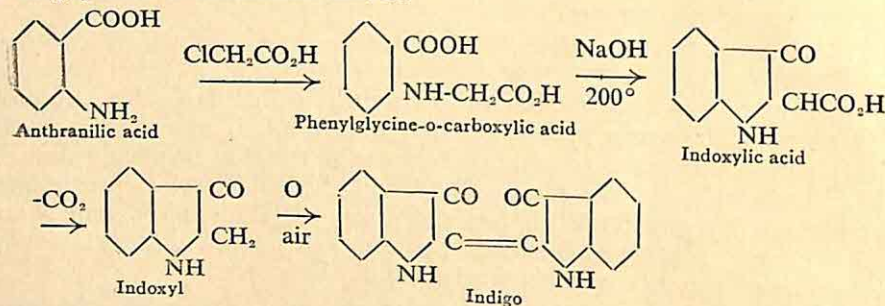
α -Methylindole, however, has no foul smell. It crystallises in plates (m.p. 95°).

Indoxyl or β -hydroxyindole, $\text{C}_8\text{H}_7(\text{OH})\text{N}$, occurs in the indigo plant as a glucoside *indican*, and in the urine of the mammals as potassium indoxyl sulphate (*urinary indican*). Indoxyl may be obtained by potash fusion of phenylglycine-*o*-carboxylic acid in absence of air. It is also formed when indigo is fused with potash or indican is hydrolysed by an enzyme. It is unstable. Indoxyl forms yellow crystals (m.p. 85°), soluble in water and alkalis. In alkaline solution, it is readily oxidised by air to indigo.





Heumann's process (1890) with cheap anthranilic acid from naphthalene (p. 414), proved a commercial success.



The present-day method consists in cyclisation of phenylglycine, $\text{C}_6\text{H}_5\text{NHCH}_2\text{COOH}$, made by hydrolysing phenylglycine nitrile, $\text{C}_6\text{H}_5\text{NHCH}_2\text{CN}$, (obtained from aniline, HCHO and NaCN), with sodamide to indoxyl. The latter, in alkaline solution, is oxidised to indigotin by air. Germany spent about £20,00,000 for chemical research and technical development before synthetic indigo was in the market. In 1880 India had 2800 of it (nearly $\frac{1}{3}$ in Bengal alone), the export value was £35,00,000; it fell to £60,000 in 1913. The total production in 1934-35 was only 510 tons, chiefly in Madras, and nothing in Bengal.

QUESTIONS

1. Write the constitutional formula of the following: thiophene, pyrrole, pyridine, isoquinoline, anthraquinone, amino-acetic acid and anthranilic acid. B.A., Pass, 1938, Bombay Uni.
2. Describe the synthesis of indigo from naphthalene. B.A., Pass, 1937, Bombay Uni.
3. How do you arrive at the structure of pyridine? B.Sc. Exam. 1947, Benares Hindu Uni.
4. How is pyridine obtained? Give its chemical properties. How has its structure been established? B.Sc., 1952, Nagpur Uni.
5. How has the constitution of quinoline been established? Enumerate the important properties of this compound. B.Sc. Exam. Muslim Uni., Aligarh, 1948.
6. How are quinoline and isoquinoline synthesised? What are the products formed on oxidising them by means of KMnO_4 ? B.Sc. Degree Exam. 1941, Andhra Uni.
7. Give evidences to show that pyrrole resembles aromatic compounds and possesses properties like phenol and aromatic amines. B.Sc. 1953, Rajputana Uni.

CHAPTER XLVI

THE ALKALOIDS

Plants and plant products attracted the attention of man long before organic chemistry developed into a science. The use of numerous herbs in *Ayurveda*, the oldest system of medicine, is a well-known fact. Ancient chemists broadly classified plant products into vegetable acids, vegetable bases, etc. The latter were termed *Alkaloids* meaning 'alkali-like' (cf., metaloids). These have one or more trivalent N-atoms, and form salts with acids. They are also called *nitrogen bases*. They are mostly amines, their names end in *-ine*. By alkaloids we now mean nitrogenous cyclic bases, with nitrogen in the ring, which occur in plants and only rarely in animals. This definition is not quite satisfactory inasmuch as there are the synthetic alkaloids, identical with natural ones; purine bases e.g., caffeine, theobromine, etc. do not behave like true alkaloids in many respects and are not included among the latter; adrenaline (an animal alkaloid) and ephedrine have nitrogen in the side-chain. Broadly, the alkaloids are derivatives of pyridine, quinoline and isoquinoline but there are exceptions as well, e.g., hygrine is a pyrrolidine compound.

In 1803 Derosne isolated a crystalline substance from opium and called it 'opium salt'; its basic property, however, escaped his notice. In 1805 Sertürner, a German apothecary, obtained it independently, noted its basic character and named it 'morphium'. In 1818, Pelletier and Caventou discovered strychnine in *Nux vomica*; next year, they obtained brucine and a year after, isolated quinine and cinchonine from cinchona bark. Since then many new alkaloids have been isolated and described; to-day nearly 800 are known.

Occurrence.—Plants with alkaloids are widely distributed in nature. Alkaloids occur almost exclusively in dicotyledons, and scarcely in monocotyledonous plants. They are found in cell sap (e.g., opium), leaves (e.g., coca), stems, fruits (e.g., piperine of black pepper), seeds (e.g., nux vomica), bark (e.g., quinine), roots (e.g., berberine), etc. Seldom does an alkaloid occur alone, opium contains at least 20 and new ones are still being isolated therefrom. Closely related alkaloids are generally found in the same plant. They are mostly present as salts, usually with tannic, malic, citric, oxalic, and rarely with acetic and lactic acids. Alkaloids of the same group are found combined with the same acid, e.g., aconite alkaloids with aconitic acid, cinchonine alkaloids with quinic acid.

Classification.—This is done according to the source (e.g., *opium* alkaloids) or the heterocyclic nucleus alkaloids contain. But there are complex alkaloids with two or more rings, and many others of unknown constitution. Broadly, they are

- (i) Hydroxyphenyl alkylamine & phenyl hydroxy-alkylamine alkaloids: e.g., adrenaline, ephedrine.
- (ii) Pyridine alkaloids: e.g., nicotine, piperine, coniine.
- (iii) Pyrrolidine alkaloids: e.g., hygrine, stachydrine.
- (iv) Tropane alkaloids: e.g., cocaine, atropine.
- (v) Quinoline alkaloids: e.g., quinine, cinchonine, strychnine, brucine.

(vi) Isoquinoline alkaloids: e.g., narcotine, papaverine.

(vii) Phenanthrene alkaloids: e.g., morphine, codeine.

Properties.—The alkaloids usually contain C, H, O and N, a few like nicotine, coniine, etc., have no oxygen; these are usually liquid. Alkaloids are mostly crystalline solids. They are colourless, some e.g., berberine are yellow. They are insoluble in water (nicotine and coniine are exceptions) but dissolve in neutral organic solvents such as benzene, ether, chloroform, ethanol, carbon tetrachloride, amyl alcohol, etc. They readily form crystalline salts with mineral acids, are extracted from plants with dilute HCl or H_2SO_4 . Their salts have the opposite solubilities. The alkaloids are as a rule bitter, some e.g., piperine are tasteless. Majority of them are optically active, usually lævo-rotatory, a few e.g., coniine are dextrorotatory. They are mostly odourless; nicotine, coniine, etc., have a strong odour. Quinine, brucine, etc., are sometimes employed for the resolution of racemic acids (p. 259) and *d*-tartaric acid for resolving a racemic mixture of alkaloids. Alkaloids are characterised by their physiological action; many are deadly poisons but in minute doses, serve as valuable drugs.

Isolation.—Only a few can be extracted with organic solvents. In many cases, they are to be set free by alkali—lime or baryta—before extraction with solvents. They are converted into water-soluble salts with dilute HCl or H_2SO_4 , filtered and the filtrate made alkaline. Free alkaloids are then recovered by filtration, extraction with a suitable solvent, or steam-distillation. They may also be separated in the form of sparingly soluble salts. Resins and colouring matters may be removed by oxidation or adsorption on charcoal.

Tests.—(i) In presence of HCl, alkaloids yield yellow, crystalline ppt. of $BHAuCl_4$ with auric chloride, $AuCl_3$ (or platinic chloride, $PtCl_4$), B being the alkaloid. The alkaloid may be identified from the m.p. of this derivative.

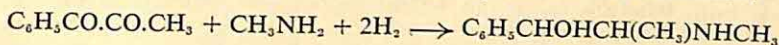
(ii) Alkaloids give white or yellowish ppt. with a solution of mercuric iodide in pot. iodide (*Mayer's reagent*). 1 part of strychnine in 80,000 parts of water may thus be detected. They also yield white or yellowish ppt. with a dilute solution of iodine in pot. iodide (*Wagner's reagent*); an orange-red ppt. with potassium-bismuth-iodide (*Dragendorff's reagent*); a white or yellowish amorphous ppt. with phosphotungstic acid (*Scheibler's reagent*); etc.

(iii) Colorations are produced by many alkaloids with reagents mostly dehydrating or oxidising e.g., conc. H_2SO_4 containing a trace of HNO_3 (*Erdmann's reagent*); 1% solution of ammonium molybdate in conc. H_2SO_4 (*Froehde's reagent*) or sodium metavanadate in conc. H_2SO_4 (*Mandelin's reagent*).

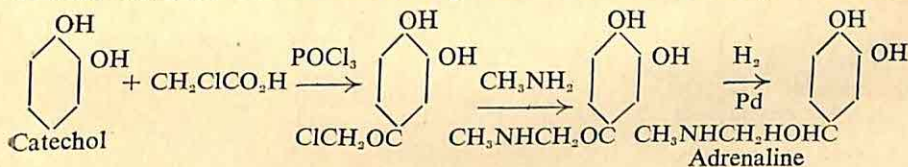
In alkaloid poisoning, e.g., with morphine, the contents of the stomach are pumped out and a liberal dose of dilute tannic acid solution is given to render the alkaloid insoluble (and so, physiologically inactive).

Ephedrine, $C_{10}H_{15}NO$, occurs in *Ephedra vulgaris* and was discovered by Nagai. The Chinese have used the herb *Ma Huang* (which contains ephedrine) as a drug for more than 5,000 years. It is a phenylalkylamine, $C_6H_5 \cdot CH(OH) \cdot CH(NH \cdot CH_3) \cdot CH_3$, (m.p. 40°) and exhibits a lævo-rotation in alcohol. It is used for increasing blood pressure, and in bronchial asthma, hay fever and cold. Ephedrine resembles adrenaline in physiological action and may be taken orally. *Pseudo-ephedrine* (m.p. 118°), a stereo-isomer, accompanies ephedrine and is

dextro-rotatory. Ephedrine was synthesised in 1929 by catalytically reducing benzoyl-acetyl in presence of methylamine in methanol:

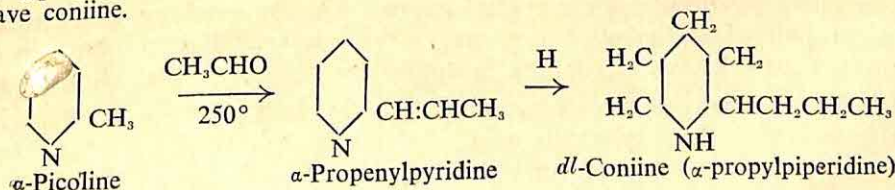


Adrenaline, epinephrine, $\text{C}_9\text{H}_{13}\text{NO}_3$ (*epi* upon, *nephros* kidney) is a hormone secreted by glands situated over the kidneys (*adrenal* at the kidney). It is the first hormone (*hormaein*, to excite) isolated in crystalline form (1901) and identified as a chemical entity and also the first to be synthesised. During emotional excitement, it is produced in large amounts. It has not been found in plants. It is extracted from supra-renal glands; synthetic adrenaline (racemic) is made from catechol. The gland product (m.p. 211°) is only slightly soluble in water. It is *l*-rotatory and physiologically 15-20 times more active than the *d*-isomer. Adrenaline gives a green colour with ferric chloride. On potash fusion, it yields protocatechuic acid and catechol. On hydrolysis with boiling alkalis, methylamine is formed. Adrenaline is used in medicine, it contracts arteries and raises blood pressure considerably; it constricts blood capillaries and stops bleeding. It is also employed in asthma, hay fever, etc. The hormone is exceedingly potent, the concentration of adrenaline in normal blood is reported to be about 1 in 2,000 million!



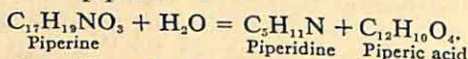
Coniine, $\text{C}_8\text{H}_{17}\text{N}$, occurs in the spotted hemlock (*Conium maculatum*) as a salt of malic acid. The plant or better, the crushed seeds are distilled with caustic soda solution and coniine is extracted from the distillate with ether. It is a colourless, poisonous (fatal dose 0.2 g.), oily liquid (b.p. 167°) which turns brown on exposure to air. It is fairly soluble in water and has a disagreeable odour recalling a mouse and a burning taste. It paralyses the respiratory system. Natural coniine is dextro-rotatory and strongly alkaline. It is the first alkaloid synthesised.

Constitution and synthesis.—Mild dehydrogenation of the alkaloid gives α -propylpyridine; pot. permanganate oxidises it to pyridine- α -carboxylic acid or α -picolinic acid. These prove a piperidine ring with a side-chain in the α -position. Reduction of coniine with hydriodic acid and phosphorus at 300° under pressure yields *n*-octane, showing an unbranched side-chain. From these and other reactions, Hofmann (1884) regarded coniine as α -propylpiperidine. Ladenburg (1886) accomplished the synthesis. α -Picoline (made by methylating pyridine with methyl iodide and heating the *N*-methylpyridine iodide, p. 459) was condensed with acetaldehyde in presence of zinc chloride to α -propenylpyridine. This, on reduction with sodium and boiling alcohol, gave coniine.

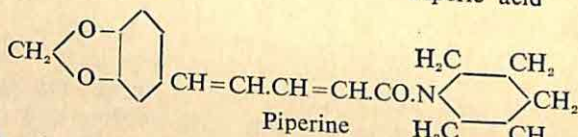
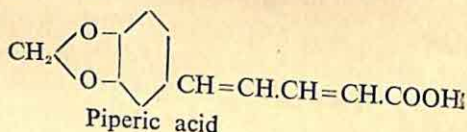
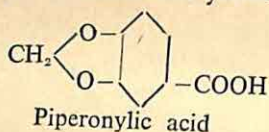


He resolved *dl*-coniine by fractional crystallisation of *dl*-coniine-*d*-tartrate; *d*-coniine was identical with the natural variety. Socrates was put to death in 399 B.C. with hemlock juice, the official poison for criminals in Greece. The toxicity of alkylpiperidines increases with the length of the side-chain, coniine is about eight times as toxic as piperidine.

Piperine, $C_{17}H_{19}NO_3$, the principal alkaloid of *Piper nigrum* or black pepper (5-9%), is obtained by heating powdered pepper with milk of lime and extracting the dried mass with ether. It forms beautiful, colourless, monoclinic crystals (m.p. 128°), practically insoluble in water. Except as a local irritant, it has no physiological activity. The sharp taste of pepper is due to the *cis*-isomer, *chavicine*. Piperine is a very weak, optically inactive base. Alcoholic potash hydrolyses piperine to piperidine and pot. salt of piperic acid, showing that it is an amide of piperic acid with piperidine.



Both piperic acid and piperidine (p. 458) have been synthesised; Rügheimer (1882) combined, by heating the acid chloride of piperic acid with piperidine in benzene solution and obtained piperine. Piperic acid, on oxidation, yields piperonylic acid.

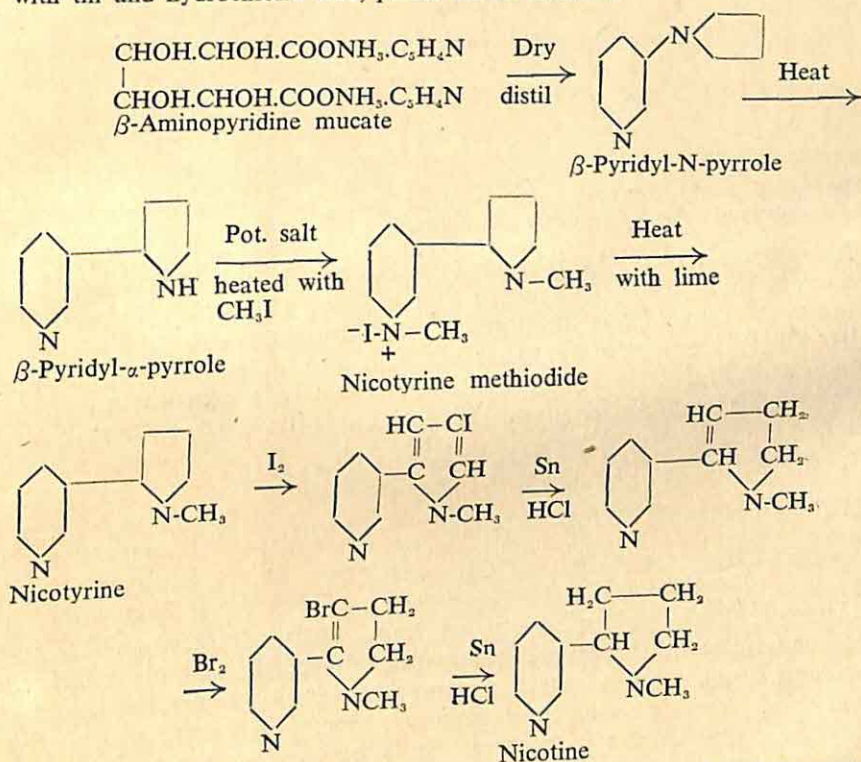


Nicotine, $C_{10}H_{14}N_2$.—The leaves of *Nicotiana tabacum* and *Nicotiana rustica* contain a number of alkaloids of which the most important is *nicotine* (from *Nicot* who introduced tobacco in France). It occurs combined with malic and citric acid; dry tobacco leaves have 0.6 to 8% of it and *rustica* 5-14%. The base is obtained by distilling the powdered tobacco leaves and stems with milk of lime and extracting the distillate with ether or petroleum ether. Crude nicotine is purified through the oxalate. Nicotine, a colourless oil (b.p. 247°), darkens on exposure to air and is volatile in steam. It is *laevo*-rotatory, but its salts are *dextro*-rotatory. It is miscible with water in all proportions below 60° and above 210° , and has a limited solubility in between. It is soluble in alcohol, ether or ligroin. It has a disagreeable odour, and is a deadly poison—the fatal dose for man being about 40 mg. *l*-Nicotine contracts the blood vessels and the intestine and also stimulates the central nerves. During smoking of tobacco, about half of the nicotine appears in the smoke. The sulphate is a contact insecticide. *d*-Nicotine is much less poisonous than *l*-nicotine.

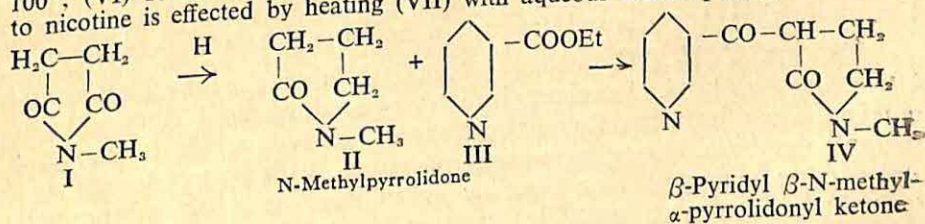
Pot. permanganate or conc. nitric acid oxidises nicotine to nicotinic acid or β -pyridine-carboxylic acid. So it is a β -derivative of pyridine. It also forms two isomeric quaternary compounds, showing the presence

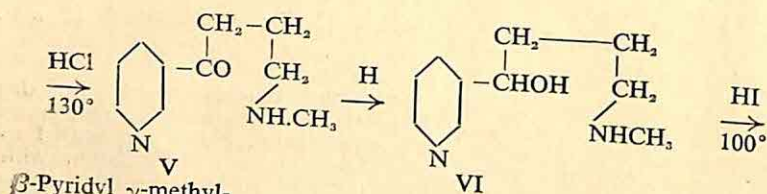
of two tertiary amino groups. A. Pictet (1903) synthesised it and resolved into *d*- and *l*-forms.

With mucic acid, β -aminopyridine gives the mucate which, on dry distillation, forms β -pyridyl-N-pyrrole. This, on heating strongly, rearranges to β -pyridyl- α -pyrrole. Its potassium salt and methyl iodide are heated to obtain a methyl derivative, nicotyrine methiodide, which, on distillation with lime, yields nicotyrine. It is iodinated with iodine, and the resulting iodo-compound reduced with tin and hydrochloric acid to a hydro-derivative. This forms bromonicotine with bromine in glacial acetic acid, which, on reduction with tin and hydrochloric acid, passes on to nicotine.

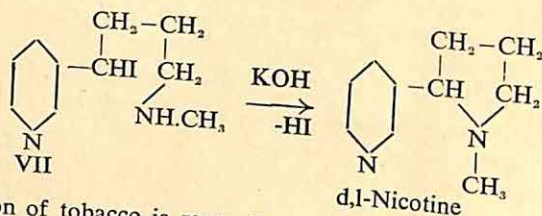


Späth (1928) did it more conclusively but differently. Methylsuccinimide (I), on electrolytic reduction, gives N-methylpyrrolidone (II). This is condensed with ethyl nicotinate (III) in presence of sodium ethoxide in benzene solution to (IV). On heating with fuming hydrochloric acid at 130°, (IV) yields (V) by hydrolysis and loss of carbon dioxide. Reduced with zinc dust and alcoholic potash, (V) passes on to (VI), a hydroxy derivative. With hydriodic acid at 100°, (VI) forms (VII), iodine replacing the -OH group. Final ring closure to nicotine is effected by heating (VII) with aqueous caustic potash.





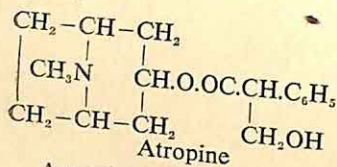
β -Pyridyl γ -methyl-amino-*n*-propyl ketone



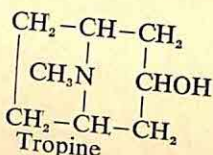
d,l-Nicotine

The world production of tobacco is more than 2 million tons corresponding to 66-70 thousand tons of nicotine alkaloids.

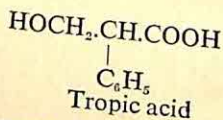
Atropine, $\text{C}_{17}\text{H}_{23}\text{NO}_3$, is present in deadly nightshade (*Atropa belladonna*), henbane (*Hyoscyamus niger*), and thorn apple (*Datura stramonium*). The last is an annual plant indigenous to India. The powdered belladonna root is made alkaline and extracted with ether to obtain atropine. It is an ester which, on hydrolysis with warm baryta solution, yields tropic acid (m.p. 117°) and tropine (m.p. 63°), a basic alcohol.



Atropine



Tropine

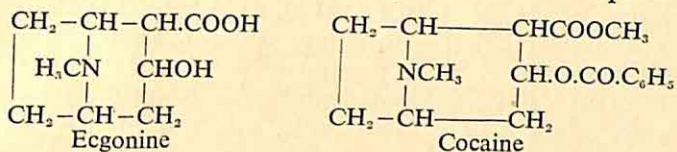


Tropic acid

Atropine forms colourless prisms (m.p. 116°), almost insoluble in water but readily soluble in alcohol or chloroform. It is a poison (0.1 g. is the fatal dose). It is a racemic, strong, tertiary base and forms well-defined salts. *Hyoscyamine*, the *l*-isomer, is racemised by warm alcoholic alkali to atropine during extraction. It is believed that atropine does not occur in the plant. Atropine (1 in 30,000 parts of water) dilates the pupil of the eye, the sulphate is used in eye surgery. It is an antidote for toadstool poisoning; it checks the flow of saliva, perspiration, etc. The sulphate is also a local anaesthetic. The *l*-isomer is more active physiologically than the racemic. Atropine was synthesised by Ladenburg in 1880. *Datura*, *hyoscyamus*, etc., were notorious for furnishing the Sorcerer's drugs in the Middle Ages as they produce hallucination. Even now, these are chewed or smoked in India, South America, etc.

Cocaine, $\text{C}_{17}\text{H}_{21}\text{NO}_4$, occurs (about 1%) in coca leaves (*Erythroxylon coca*), used by S. American Indians as a stimulant. Much of it is obtained from Java, mainly as the cinnamyl derivative which has little therapeutic value. Coca leaves are macerated with aqueous soda ash and cocaine extracted with benzene or toluene. It is crystalline and strongly basic, almost insoluble in water but soluble in alcohol, ether

or chloroform. Cocaine (m.p. 98°) is lævorotatory. It is the methyl ester of benzoylecgonine and is closely related to atropine.



Alkalis or mineral acids hydrolyse it to *l*-ecgonine (tropine-carboxylic acid), benzoic acid and methyl alcohol. With boiling water, benzoylecgonine and methanol result. Willstätter synthesised cocaine in 1923.

Cocaine paralyses the peripheral nerves and is a local anæsthetic in dentistry and minor surgical operations. Taken internally, it deadens hunger, and increases physical and mental power but the after-effect is extreme depression. It is a drug of addiction. Cocaine increases the body temperature considerably. *Novocaine*, $\text{H}_2\text{N}.\text{C}_6\text{H}_4.\text{CO}.\text{OCH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$, a synthetic product, which is a much less toxic and also cheaper anæsthetic, has replaced cocaine. *Theobroma cacao*, the source of cocoa and chocolate, is quite different from the plant that gives cocaine.

Quinoline alkaloids.—The cinchona alkaloids are the most notable of the group. More than thirty occur combined with quinic and cinchotannic acid in the stem, branches and root-bark of the species *Cinchona*, the most important being cinchonine and quinine. Cinchona bark was used as a febrifuge about three centuries back, and though its original home is South America (known as 'fever tree' there), it is now extensively cultivated in Java and India. Quinine which is methoxycinchonine, is much more effective in malaria than cinchonine.

Cinchona plantations in India are at Mangpoo and Mansong in the Darjeeling district of West Bengal under the State Government. There is another in Madras. Java is now the greatest cinchona-producing country of the world. India requires about 600,000 lb. of quinine annually but produces about 90,000 lb. only. The world production of quinine (about 600 tons) falls short of the requirement and hence the need for synthetic anti-malarials. In 1638 Anna Cinchon, wife of the Spanish viceroy of Peru, was cured of malaria with the bark of this plant which was named *cinchona*. The alkaloids occur in the bark, specially in lower parts of the trunk (2-10%). This in some species may contain 18.5% of quinine (as sulphate).

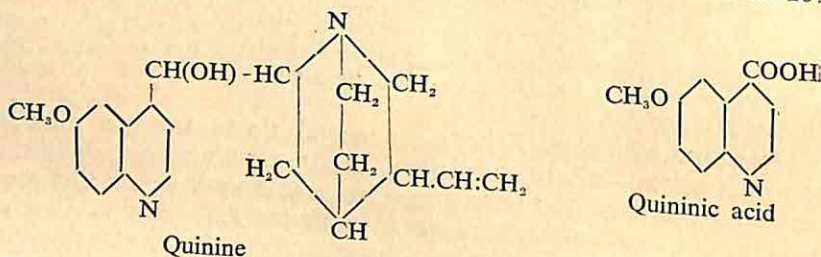
Quinine, $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2$, was discovered in cinchona bark by Pelletier and Caventou in 1820.

Preparation.—Dried cinchona bark is pulverised and thoroughly mixed with slaked lime (30% by wt.) and 5% caustic soda solution (90% by wt.), and evaporated to dryness. The dark brown mass is extracted with boiling, heavy petroleum, benzene or toluene. The extract is agitated with hot, dilute H_2SO_4 , the alkaloids dissolve as neutral sulphates. The hot solution is neutralised with soda ash and allowed to cool. Crystals of sparingly soluble quinine sulphate separate, minor alkaloids remaining in solution. It may be decolorised with animal charcoal, and recrystallised from water. The free base is obtained by treating the sulphate (in dilute H_2SO_4) with dilute sodium carbonate and recrystallising. Salts other than the sulphate are prepared from the free base.

Quinine crystallises in white needles with three molecules of water (m.p. 57°). It melts at 177° when anhydrous. It is almost insoluble in water but readily soluble in ether, alcohol or chloroform. Quinine, as well as its salts has an extremely bitter, persistent taste. It is a lævo-

rotatory, $[\alpha]_D = -158^\circ$, weak, di-acidic base and forms salts with acids. The common salts are the sulphate, $(C_{20}H_{24}N_2O_2)_2H_2SO_4 + 8H_2O$, and the hydrochloride, $C_{20}H_{24}N_2O_2HCl + 2H_2O$. $Q \cdot H_2SO_4 + 7H_2O$, $Q \cdot 2H_2SO_4 + 7H_2O$ as well as $Q \cdot 2HCl$ (Q = quinine) are also known. Acid salts are more soluble in water than normal salts of H_2SO_4 or HCl . A very dilute solution of the sulphate exhibits a beautiful blue fluorescence. Quinine, in small doses, is a tonic, but it is highly toxic.

Quinine, a tertiary diamine, combines with two mols. of methyl iodide. It has a hydroxyl and a methoxy group. Quinoline is obtained from quinine by distilling with caustic potash (p. 460). On oxidation with chromic acid, quininic acid, quinic acid, $C_6H_7(OH)_4COOH$, etc. are formed. Königs suggested the following structure for quinine; a synthesis by Woodward and Doering (reported from U.S.A. in 1944) confirmed it.



Euquinine (ethylquinine carboxylate), *Saloquinine* (the salicylic ester), tannate of quinine, etc. are tasteless. Quinine sulphate produces a characteristic ringing in the ear and in large doses may cause deafness; the hydrobromide is better. *Plasmoquine* (a quinoline compound), *Atebrin*, *Mepacrine* (an acridine derivative) and *Paludrine* (chloroguanide) are more effective and less toxic substitutes.

Tests.—(i) On adding a slight excess of chlorine-water and then ammonia to the solution of a quinine salt, a green ppt. is obtained, soluble in excess of ammonia with an emerald green colour.

(ii) A dilute (0.5%) solution of quinine sulphate in dilute sulphuric acid shows blue fluorescence which is discharged by dilute hydrochloric acid.

Cinchonine, $C_{19}H_{22}ON_2$.—The mother-liquor, after separation of quinine, is made alkaline with caustic soda. The precipitate is dissolved in the least quantity of boiling alcohol, from which cinchonine crystallises on cooling. It forms white prisms (m.p. 264°) that sublime readily. It is dextro-rotatory, $[\alpha]_D = 234^\circ$, slightly soluble in water and highly soluble in alcohol or chloroform. Cinchonine forms salts like quinine. Chromic or nitric acid oxidises it to cinchoninic acid or γ -quinoline-carboxylic acid. Unlike quinine, cinchonine and its salts give no colour with chlorine-water and ammonia, nor does the sulphate exhibit fluorescence in dilute solution.

Strychnine and **brucine** (which is dimethoxy-strychnine) occur together in the seeds of *Strychnos nux vomica* or Saint Ignatius' beans (2.3%). The ground seeds are macerated with water and slaked lime and the alkaloids are extracted with benzene or toluene. Both yield quinoline and indole on potash fusion. In alcoholic solution, $[\alpha]_D$ for strychnine is -110° and for brucine, -80° . R. Robinson in 1946

suggested a constitution for strychnine, supported by X-ray analysis; R. B. Woodward has confirmed it in 1954 by synthesis (p. 476). Both alkaloids are employed for resolving racemic acids.

The mono-acid base *strychnine*, $C_{21}H_{22}O_2N_2$, is a colourless, crystalline solid (m.p. 284° with decomposition), almost insoluble in water but highly soluble in chloroform. It is extremely poisonous and causes death after tetanic spasms. In very minute doses strychnine is a tonic and a heart and respiratory stimulant. It kills vermin and other smaller animals. Half-a-grain of strychnine sulphate may prove fatal. Even 1 in 5,00,000 of water has a very bitter taste.

Test.—Finely powdered pot. dichromate is sprinkled over a solution of strychnine in conc. sulphuric acid, a violet coloration, first produced, changes gradually to red, and finally, to yellow.

India is the largest producer of strychnine salts; her annual production is estimated at 15,000 lb.

Brucine, $C_{23}H_{26}O_4N_2 \cdot 4H_2O$, is a colourless, crystalline mono-acid base, melting at 178° when anhydrous. It has no therapeutic value (cf., quinine and cinchonine). Brucine is more soluble in alcohol and water and less poisonous than strychnine. It is a constituent of rat poisons.

Test.—A deep orange colour is produced when nitric acid or a nitrate is added to a solution of brucine in conc. H_2SO_4 . The colour turns violet on adding a little stannous chloride solution. This is also a delicate test for nitrates.

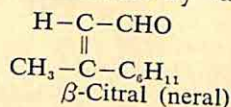
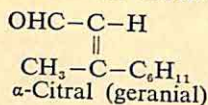
Emetine, $C_{29}H_{40}N_2O_4$, an amorphous powder (m.p. 74°), occurs in the root of *Psychotria ipecacuanha* and is extracted from the ground root with alcohol or benzene. It is a powerful emetic, hence the name (Greek *emetikos*, vomit). It is a remedy for amebic dysentery. A constitution for the alkaloid has been suggested in 1948 by R. Robinson, which contains two 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline nuclei and an ethyl group.

Morphine, $C_{17}H_{19}O_3N$.—The juice of some poppy (*Papaver somniferum*) heads contains some 25 alkaloids as salts of meconic and lactic acid; the most important is morphine. The dried juice from unripe capsules is *opium* (Greek *opion* poppy juice) from which morphine was separated in 1805 by Sertürner, a German apothecary. It is the first alkaloid to be isolated.

Opium, triturated with calcium chloride solution to a thin paste, is extracted with hot water. The alkaloids form soluble hydrochlorides; calcium meconate and lactate precipitate. The filtrate is concentrated in vacuo: narcotine and papaverine are removed with sodium acetate solution. Morphine is precipitated from the filtrate with lime and ammonium chloride. The crude product is washed with benzene and converted into the hydrochloride with HCl. It is recrystallised from water. The free base may be liberated from an aqueous solution of its salt with ammonia. Opium contains about 10% of morphine on an average.

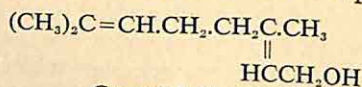
Monohydric crystals (m.p. 254°) of morphine are very slightly soluble in water and cold alcohol but unlike most alkaloids, dissolve in alkalis. Morphine has a phenolic -OH, a $-CH_3$ linked to nitrogen, and a secondary alcoholic -OH group. It is a tertiary, mono-acid base and forms crystalline salts with acids. The sulphate, $M_2H_2SO_4 \cdot 5H_2O$, and the hydrochloride, $M \cdot HCl + 3H_2O$, (M = morphine) are soluble in water. It is lævo-rotatory, $[\alpha]_D = -131^\circ$ in metha-

This constitution of citral has been confirmed by various syntheses.

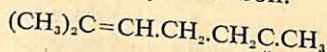


Treated with dilute H_2SO_4 and KHSO_4 , citral loses water and gives *p*-cymene (p. 334). Both α - and β -citral boil at 118° under 20 mm pressure.

Geraniol, $\text{C}_{10}\text{H}_{17}\text{OH}$, a primary alcohol, occurs in varying amounts in the oils of geranium, rose, citronella and lemongrass. *Nerol*, its *cis* stereoisomer, is found in neroli oil and bergamot oil. Both have rose-like odour and are used as perfumes. Geraniol is a useful insect attractant (into traps). Citral on reduction gives geraniol. Dilute H_2SO_4 converts both geraniol and nerol into cyclic terpenes, α -terpineol and terpene hydrate, nerol much more rapidly than geraniol. Nerol readily loses water and forms dipentene, a cyclic hydrocarbon.



Geraniol (trans)
(b.p. 230°)

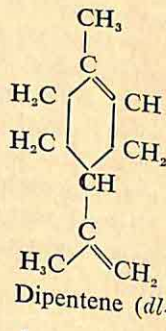
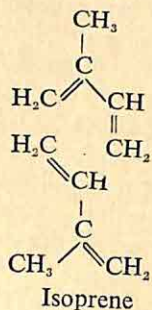


$$\begin{array}{c} || \\ \text{HOH}_2\text{C}.\text{C}.\text{H} \end{array}$$

Nerol (*cis*)
(b.p. 225°)

Linalool, $(\text{CH}_3)_2\text{C}=\text{CH}.\text{CH}_2.\text{CH}_2.\text{C}(\text{CH}_3)\text{OH}.\text{CH}=\text{CH}_2$, a tertiary alcohol (b.p. 198°), is isomeric with geraniol and nerol; it occurs in oil of linaloa, a Mexican wood, and oil of lavender.

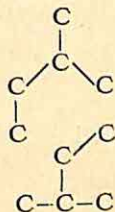
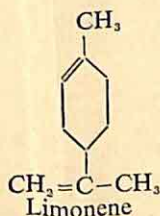
Dipentene, *dl*-limonene, $\text{C}_{10}\text{H}_{16}$, the most important monocyclic terpene, is a dimer of isoprene. Natural rubber, on dry distillation, yields about 10% of dipentene, possibly formed from isoprene, the main product of distillation. Dipentene gives back isoprene on pyrolysis. Pinene, main constituent of turpentine oil, gives dipentene on heating at 250° . Pinene is isomeric with dipentene. By reaction with H_2SO_4 , geraniol forms dipentene by cyclization. By way of a Diels-Alder reaction, isoprene can be dimerized to dipentene:



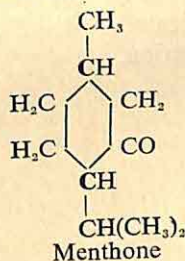
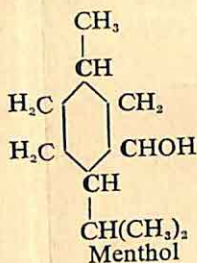
Limonene has a pleasant, citrus-like odour; *d*-limonene occurs in lemon, bergamot, and orange oils; *l*-limonene is found in the needles of Douglas fir. *dl*-Limonene or dipentene is present in lemongrass oil and turpentine. The C in thick type in limonene is asymmetric and accounts for the optical activity. *d*- and *l*-limonene boil at 177° and

have $[\alpha]_D = \pm 125^\circ$. The presence of isoprene or isopentane units,

C-C-C-C, in terpenes, e.g., limonene, has led to the "isoprene rule"; even complex terpenes can be hypothetically constructed from such units and any deduced structure of this type which does not obey the rule, is suspected.



Menthone, $C_{10}H_{18}O$, occurs in *d*- and *l*-forms in some essential oils, *l*-menthone is found in peppermint oil and *d*-menthone in pennyroyal oil. Both are liquids (b.p. 207°) having peppermint odour. Menthol, the main component of oil of peppermint, is a secondary alcohol which gives menthone, a ketone, on oxidation with $K_2Cr_2O_7$ and H_2SO_4 . Menthone forms menthol on reduction with sodium and ethyl alcohol. *l*-Menthone has $[\alpha]_D = -20^\circ$; it was synthesised long before it was first found in Russian peppermint oil.

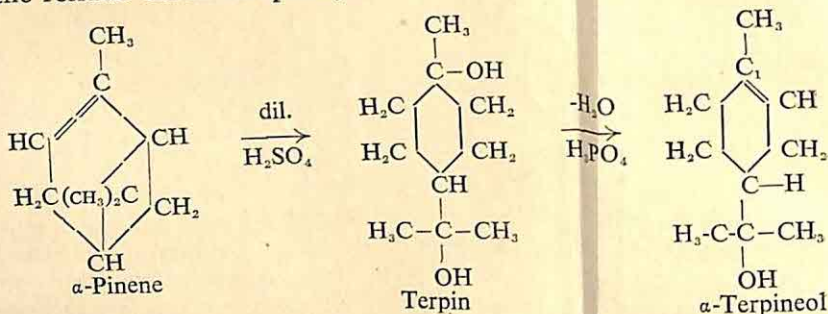


Menthone has two asymmetric C atoms (in thick type) and should exist in four active forms; the *l*-isomer occurs more abundantly in nature.

***l*-Menthol**, $C_{10}H_{19}OH$, the most important component of peppermint oil, is a solid (m.p. 43°) secondary alcohol. It was known and used in Japan some 2000 years ago. Menthol is commercially made from peppermint oil by cooling, pressing, and recrystallising. It has 3 asymmetric C-atoms and should exist in 8 isomeric forms; *l*-menthol, the naturally occurring isomer, is widely used as an antiseptic, and stimulant. It is used in nasal sprays, gargles, toilet creams and ointments. It relieves headache in colognes. Synthetic menthol (*dl*-) is made by catalytic hydrogenation of thymol (p. 393). Menthol forms needles and has a pleasant peppermint odour and a cooling taste. HI reduces it to hexahydro-*p*-cymene and chromic acid oxidises it to menthone.

α -Terpineol, $C_{10}H_{17}OH$, is a colourless, solid (m.p. 35°) tertiary monohydric alcohol, widely found in nature in *d*-, *l*- and *dl*-forms.

It is a component of petitgrain, neroli, cardamom, cajuput and marjoram oils. Terpin, $C_{10}H_{20}O_2$, a dihydric tertiary alcohol, on dehydration with mineral acids, forms α -terpineol. Limonene takes up a mol. of water in presence of dilute H_2SO_4 and passes on to α -terpineol. Industrially, α -pinene, $C_{10}H_{16}$, of turpentine oil is hydrated to terpin and then dehydrated to α -terpineol with phosphoric acid. Turpentine, on steam-distillation, yields oil of turpentine and a non-volatile residue called *colophony*.



Three other structural isomers having the $-OH$ group in C_1 , viz., terpineol-1, β - and γ -terpineol, are also formed simultaneously but in smaller amounts. Commercial terpineol is a mixture of all the four isomers. Having the odour of lilac, it is largely used in making perfumes. Heated with $KHSO_4$, α -terpineol forms dipentene, $C_{10}H_{16}$, by dehydration.

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